

PRACTICAL WORKBOOK

33

CHEMISTRY (HONOURS)



UGBS, CHEMISTRY
UNIVERSITY OF CALCUTTA
2015

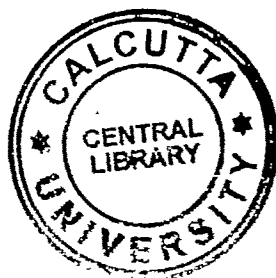
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PRACTICAL WORKBOOK

CHEMISTRY (HONOURS)

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Board of Undergraduate Studies in Chemistry
University of Calcutta
2015

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Foreword

This workbook grew out of a few seminars, intense discussions, and feedbacks from a number of teachers on an earlier draft version of the book that was sent to all the colleges under CU with honours affiliation. The whole exercise covered a period of about 2–3 years. We hope, now it has been sufficiently enriched to warrant publication. The task was monumental. It seemed virtually an impossible assignment, had the members of UGBS only been involved in the exercise. So, we invited some faculty members from different institutions within the city to actively participate in finalizing the job. We are grateful to all of them for their kind cooperation.

I take this opportunity to also thank all the other members of the Board for their prudent inputs from time to time. It is hoped that this endeavor will be beneficial to both the students and teachers of the University of Calcutta.

Kamal Bhattacharyya
Chairman, UGBS (Chemistry), CU

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Part-I (Year 1)

A few words about Inorganic Qualitative Analysis

Inorganic Qualitative Analysis has long been considered as the most intriguing part of Inorganic Chemistry. But the so-called treacherous role of this part of chemistry has been reduced appreciably as plenty of specific, sensitive and reliable reagents are now available by the use of which the hurdles underlying the work have been overcome. For the improvement of performance an analyst should also adopt the systematic approach and work with caution, care and cleanliness. A short discussion on the complete analytical work is furnished here to make the students conversant with the entire process. The discussion includes:

- (i) Writing up the conclusions in the Inference Column.
- (ii) Explanatory notes on some of the orientational tests.
- (iii) Some working hints.
- (iv) The quick systematic separation, detection and confirmation of cations avoiding the interferences from BO_3^{3-} , F^- and PO_4^{3-} .
- (v) Some guidelines for the analysis of the insoluble materials.

(i) Some typical experiments along with observation and inference are presented below to provide the students some ideas on "how to write the conclusions in the inference column".

Experiment	Observation	Inference
A. Dry heating of the sample	a. Formation of a white sublimate	H_3BO_3 , S (derived thiosulfates)
	b. Yellow when hot, white when cold	Possible presence of ZnO , Zn^{2+} – salts
	c. Yellow-brown when hot, white when cold	May be SnO_2
	d. Formation of a black mass from a coloured sample	Probably Ni^{2+} , Co^{2+} , Cu^{2+} and Mn^{2+} salts
	e. Transformation of the red sample into i) a green yellow mass ii) a black mass	May be $\text{K}_2\text{Cr}_2\text{O}_7$ May be $\text{K}_3\text{Fe}(\text{CN})_6$
	f. Evolution of brown fumes giving no colour with starch solution	May be nitrates and nitrites of polyvalent metal ions

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Experiment	Observation	Inference
	g. Evolution of brown fumes giving yellow orange colour with starch	May be ($\text{Br}^- + \text{oxidant} + \text{acidic oxide}$), ($\text{BrO}_3^- + \text{reductants} + \text{acidic oxide}$)
	h. Evolution of violate vapours	Possible presence of ($\text{I}^- + \text{oxidants} + \text{acidic oxides}$)
	i. Fusible solid	Possible presence of Na^+ , K^+ – salts. Nitrates and nitrites of Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}

N.B.

- (i) Whatever may be the colour of the sample, the observations mentioned in a, f, g, h and i are always helpful in providing useful hints regarding the possible presence or absence of cations and anions.
- (ii) For white solids, in addition to the above observations, b and c are also equally useful.
- (iii) If the solid is responsive to dry heating then the cations and anions indicated by the observations are to be reported in the Inference Column. Under the circumstances it is needless to show the absence of the others.
- (iv) If the sample does not undergo notable changes during dry heating then the cations and anions susceptible to dry heating should be shown absent in the Inference Column mentioning the absence of their characteristic observations by which they are detected.

Experiment	Observation	Inference
B. Flame test. (For positive response)	Golden yellow flame Violet flame, crimson red through double blue glass And so on.	May be Na^+ – salts Possible presence of K^+ – salts (No comments should be made in the Inference Column regarding the absence of the others)
(For negative response)	Light yellow flame coloration. No golden yellow, violet, transient brick red, crimson red, apple green, bluish green flame.	Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Cu^{2+} , BO_3^{3-} may be absent

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Experiment	Observation	Inference
C. Borax bead test (Positive response)	(a) Formation of an intense blue coloured bead masking the bead colours of all the cations responsive to the test.	Co^{2+} – salts may be present. [No comments regarding the presence or absence of the other cations]
(negative response)	(b) Deep green bead (c) Formation of a bead colour not consistent with the normal bead colours of the cations detectable by the test.	May be Cr^{3+} Co^{2+} , Ni^{2+} , Cu^{2+} , Mn^{2+} or Mn^{4+} , Cr^{3+} , Fe^{3+} absent.
D. Fusion test (For positive response)	i) Formation of a green mass	May be $\text{Mn}^{2+}/\text{Mn}^{4+}$ compounds, ($\text{K}_4(\text{Fe}(\text{CN})_6 + \text{Zn}^{2+})$ mixture
	ii) Formation of a pink colour on acidification of the green mass	May be $\text{Mn}^{2+}/\text{Mn}^{4+}$ compounds
	iii) Formation of a yellow mass	May be $\text{Cr}^{3+}/\text{Cr}^{6+}$ compounds
	iv) Acetic acid extract of the yellow mass + lead acetate solution – a yellow ppt appeared	$\text{Cr}^{3+}/\text{Cr}^{6+}$ compounds present
(For negative response)	Formation of a black mass. No green or yellow mass appeared	Possible absence of $\text{Mn}^{2+}/\text{Mn}^{4+}$, $\text{Cr}^{3+}/\text{Cr}^{6+}$ compounds
E. Fluorescence test	Blue fluorescence No blue fluorescence	SnO_2 present SnO_2 may be absent
F. * HCl extract + DMG + NH_4OH (Positive response)	a. Red coloration b. Orange coloration c. Violet coloration d. Formation of a ppt kept on filter paper as a red ppt, residue when filtered	May be Fe^{2+} May be Co^{2+} May be Cu^{2+} Ni^{2+} present

* Sample + dil. HCl + KNO_2

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Experiment	Observation	Inference
(Negative response) * HCl extract + solid NH ₄ HF ₂ or NH ₄ F (excess, as masking agent) + DMG + NH ₄ OH (excess)	No coloration or precipitate formation Red ppt	Possible absence of Fe ²⁺ , Co ²⁺ , Cu ²⁺ and Ni ²⁺ Ni ²⁺ must be present
G. NaOH-extract + H ₂ S (Responsive) (Non-responsive)	Formation of a white ppt. White ppt soluble in dil H ₂ SO ₄ Absence of the above changes	May be Zn ²⁺ and/or the oxidants like BrO ₃ ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , CrO ₄ ²⁻ . May be Zn ²⁺ . Possible absence of the above ions
H. NaOH – extract + NH ₄ Cl – boiled.	White gelatinous ppt.	May be Al ³⁺ , Sn ⁴⁺ .
I. Sample + iodine – azide Do	Iodine colour discharged. Discharge of iodine colour along with effervescence.	Basic nature of the sample. May be SCN ⁻ , S ₂ O ₃ ²⁻ or S ²⁻
J. Sample + dil H ₂ SO ₄ – warmed	(i) Evolution of brown fumes (ii) Formation of red droplets in the cooler part of the test tube.	May be NO ₂ ⁻ , Br ⁻ + oxidant, BrO ₃ ⁻ + reductant. Br ⁻ + oxidant, BrO ₃ ⁻ + reductant.
K. Heating of the sample with dil H ₂ SO ₄ + Zn dust	Evolution of H ₂ S detected by blackening of AgNO ₃ paper.	May be SCN ⁻ , S ₂ O ₃ ²⁻ or S ²⁻ .
L. Sample + conc. H ₂ SO ₄ – heated, at first slowly then strongly (Positive response)	Evolution of a. Brown fumes b. Violet vapours c. Oily bubbles at the bottom of the test tube	Possible presence of Br ⁻ , BrO ₃ ⁻ , (NO ₃ ⁻ + reducing agents), (Cl ⁻ +CrO ₄ ²⁻ /Cr ₂ O ₇ ²⁻) Possible presence of I ⁻ Possible presence of F ⁻

* Sample + dil. HCl + KNO₂

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Experiment	Observation	Inference
(Negative response)	No coloured gas e.g. brown or violet coloured gas evolved Absence of oily bubbles at the bottom of the test tube	Possible absence of Br^- , BrO_3^- , (NO_3^- + reducing agents), (Cl^- + CrO_4^{2-} / $\text{Cr}_2\text{O}_7^{2-}$) and I^- Possible absence of F^- .
M. Sample + conc. H_2SO_4 – slowly heated at the initial stage and finally strongly heated with Cu-turnings (Positive response)	Evolution of brown fumes giving no colour with starch solution	May be NO_3^-
(Negative response)	Evolution of a colourless gas	Absence of NO_3^-
N. Sample + conc. H_2SO_4 + MeOH – heated and the issuing gas ignited (Positive response)	Green – edged flame	Probably BO_3^{3-}
(Negative response)	No green edged flame. Formation of a light blue flame	Possible absence of BO_3^{3-}
O. (i) HNO_3 – extract + $(\text{NH}_4)_2\text{MoO}_4$ (excess) (ii) Sample + HNO_3 – boiled until evolution of brown fumes came to an end + $(\text{NH}_4)_2\text{MoO}_4$	Formation of a blue coloured solution Yellow ppt.	Presence of PO_4^{3-} and reductant/reductants. PO_4^{3-} present
P. (i) Na_2CO_3 – extract + HNO_3 – boiled + $\text{Ba}(\text{NO}_3)_2$	White ppt	$\text{S}_2\text{O}_3^{2-}$ and or SO_4^{2-} may be present.

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Experiment	Observation	Inference
(ii) Na_2CO_3 – extract + HNO_3 – boiled–filtered to remove the ppt and then treated with $\text{Ba}(\text{NO}_3)_2$	White ppt	SO_4^{2-} present
Q. Na_2CO_3 – extract + HNO_3 until faintly acidic – boiled + AgNO_3 .	(i) Formation of a white ppt. (ii) ppt soluble in dil NH_4OH	May be Cl^- , SCN^- , BrO_3^- and $\text{Fe}(\text{CN})_6^{4-}$ May be Cl^- , SCN^- or BrO_3^-
R. Na_2CO_3 extract + HCl (until acidic) – slowly boiled and then treated with FeCl_3 + $\text{K}_3\text{Fe}(\text{CN})_6$ (Positive response) (Negative response)	Formation of a blue ppt. No blue coloration or blue ppt formation. A brown colour appeared.	Possible presence of S^{2-} , $\text{S}_2\text{O}_3^{2-}$, I^- and $\text{Fe}(\text{CN})_6^{4-}$ Possible absence of S^{2-} , $\text{S}_2\text{O}_3^{2-}$, I^- and $\text{Fe}(\text{CN})_6^{4-}$
S. Na_2CO_3 extract + HCl until acidic (boiled) + KI	Formation of a brown coloured solution.	May be $\text{NO}_2^-/\text{NO}_3^-$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- , BrO_3^- or Cu^{2+} (Cu^{2+} can be present in Na_2CO_3 extract due to the formation of $\text{Na}_2[\text{Cu}(\text{CO}_3)_2]$ and $\text{Fe}(\text{CN})_6^{3-}$ (if excess HCl is used up for acidification, $\text{Fe}(\text{CN})_6^{3-}$ becomes highly oxidizing)
T. Na_2CO_3 extract + HCl (until acidic) + FeCl_3 (Positive response) (Negative response)	a. Formation of a blue ppt. b. Blood red colouration Formation of a light green ppt	Probably $\text{Fe}(\text{CN})_6^{4-}$ and $(\text{Fe}(\text{CN})_6^{3-} + \text{reducing agents})$ Possible presence of SCN^- Absence of $\text{Fe}(\text{CN})_6^{4-}$ and $(\text{Fe}(\text{CN})_6^{3-} + \text{reducing agents})$, SCN^-

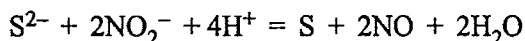
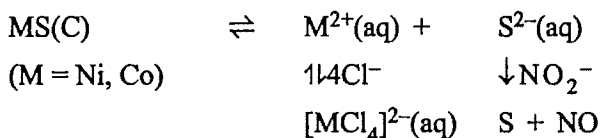
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(ii) Explanatory notes on some of the orientational tests:

(a) Use of HCl + KNO₂ for the preparation of HCl extract

Substances which are soluble in boiling aqua regia (HCl + HNO₃ = 3 : 1) can be dissolved readily in HCl + KNO₂. Aqua regia contains a complexing agent (Cl⁻) and an oxidant (Cl₂) formed during boiling: $\text{HNO}_3 + 3\text{HCl} = \text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O}$.

Materials like NiS and CoS, which have very low solubility product values, can be dissolved with the help of complexation and oxidation:



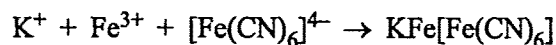
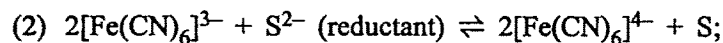
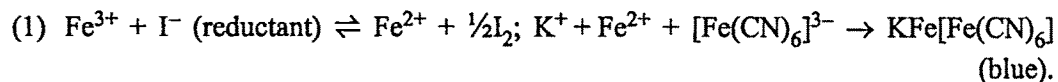
The equilibrium can be shifted to the right by the above mechanism and dissolution of the sulfides will take place.

Other mixtures which can serve the purpose of aqua regia are HCl + X₂ (X = Cl, Br, I), HCl + H₂O₂, HCl + ClO₃⁻, etc.

In the laboratory, the use of aqua regia should be avoided as far as practicable since the mixture has various adverse physiological effects.

(b) Test for reducing agents with FeCl₃ + K₃Fe(CN)₆:

The above reagent is brown in colour due to the formation of Fe[Fe(CN)₆] by which both soluble as well as insoluble reducing agents can be detected decisively as an intense blue colour is produced when the test is positive. Both Fe³⁺ and [Fe(CN)₆]³⁻ may undergo reduction:



In actuality, Fe³⁺ and [Fe(CN)₆]³⁻ are not reduced at the same rate by the reductants and consequently the blue colour always appears in presence of reducing agents.

(3) The test, Na₂CO₃ extract + HCl (until acidic) + KI is employed for the detection of oxidizing agents which may be present in the sample. (FeSO₄ + NH₄SCN) mixture is also an excellent reagent for the identification of oxidizing agents which produces a deep red colour due to the oxidation of Fe²⁺ to Fe³⁺. This test becomes somewhat

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handicapped as, in presence of SCN^- , Fe^{2+} is rapidly oxidized to Fe^{3+} by air. This is why KI is preferable to the above reagent as I^- is oxidized to I_2 at a slower rate than Fe^{2+} .

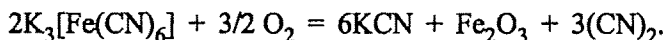
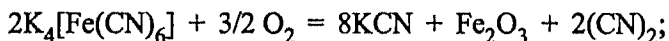
(iii) Some working hints :

(a) Heating of sample with conc. H_2SO_4 :

To carry out this experiment, the students should note carefully the action of dil H_2SO_4 with the sample. If this reaction occurs with gas evolution, then before adding conc. H_2SO_4 heating with dil H_2SO_4 should be continued until gas evolution ceases otherwise there will be violent reaction with conc. H_2SO_4 which may lead to explosion. Moreover, due to violent reaction, it will be very hard to conclude decisively on the presence or absence of anions reactive with conc. H_2SO_4 . Similar procedures must also be followed for the tests, heating of sample with conc. $\text{H}_2\text{SO}_4 + \text{MeOH}$ and heating of sample with conc. $\text{H}_2\text{SO}_4 + \text{Cu}$ – turnings.

(b) Removal of interfering $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ from the sample :

As $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ can precipitate many cations even in acid medium, these two anions if detected in the preliminary tests or by the tests by which they are detected then these are to be removed from the sample otherwise the detection and confirmation of cations will be very much problematic. Removal can be achieved by simple heating of the sample in an ignition tube:

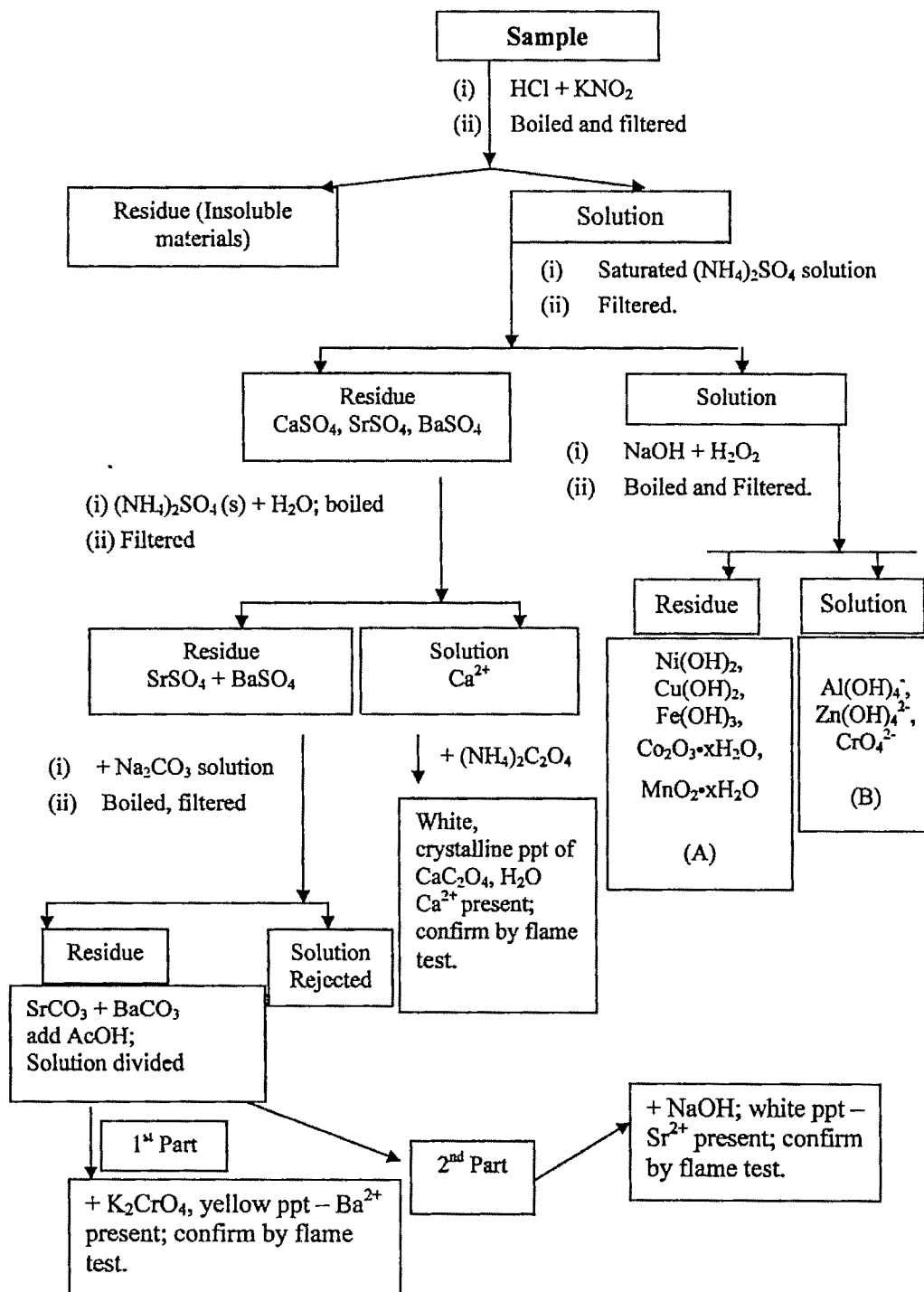


Strong heating should be continued for about 10 minutes. The residue left in the ignition tube should now be boiled with $\text{HCl} + \text{KNO}_2$ and the solution so formed should be utilized for the detection of cations.

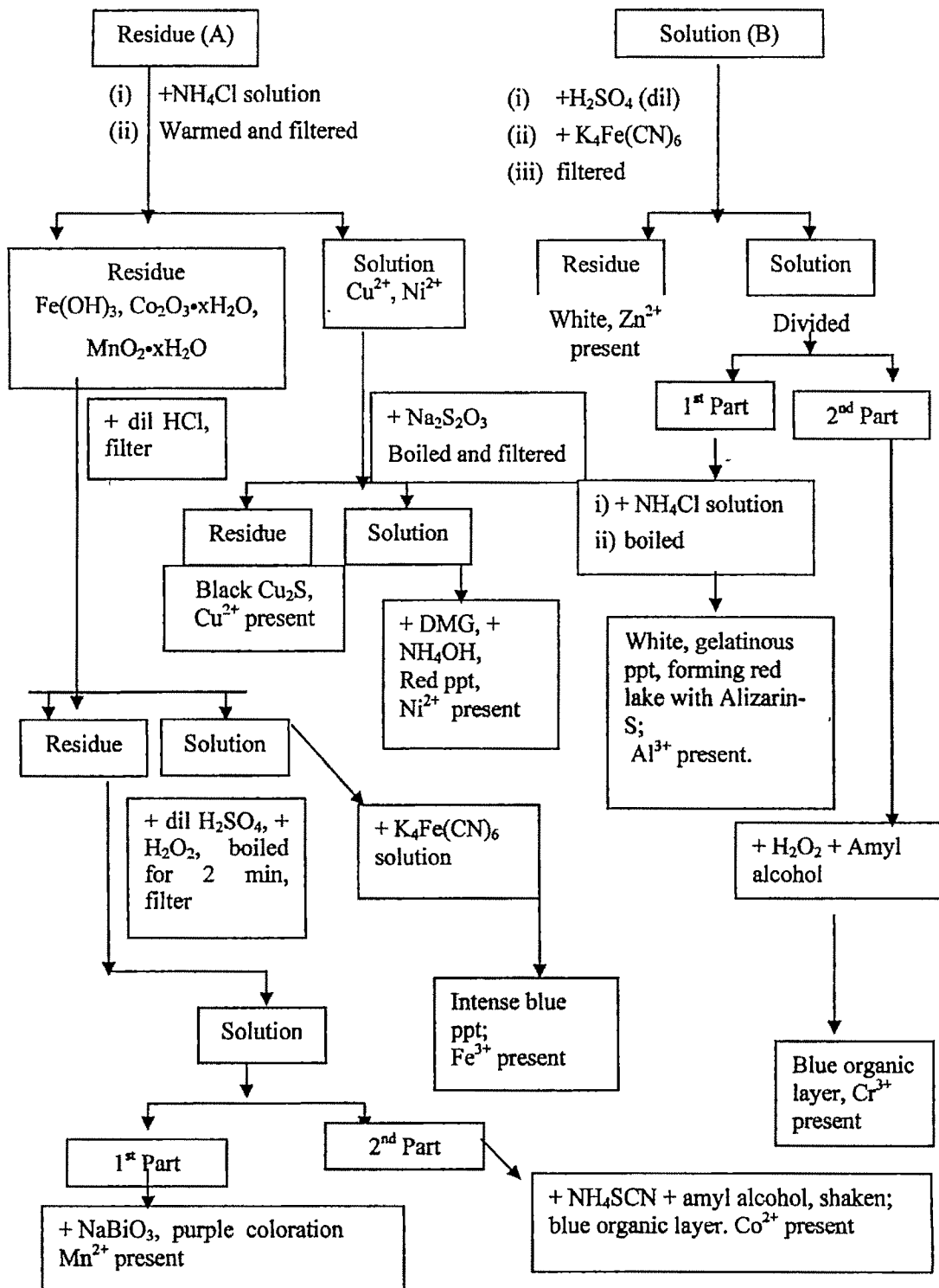
(iv) Separation, detection and confirmation of cations:

See the group separation table below; separately, detection of Na^+ or K^+ may be found. Detection of cations in insoluble materials is discussed finally.

Group Separation Table



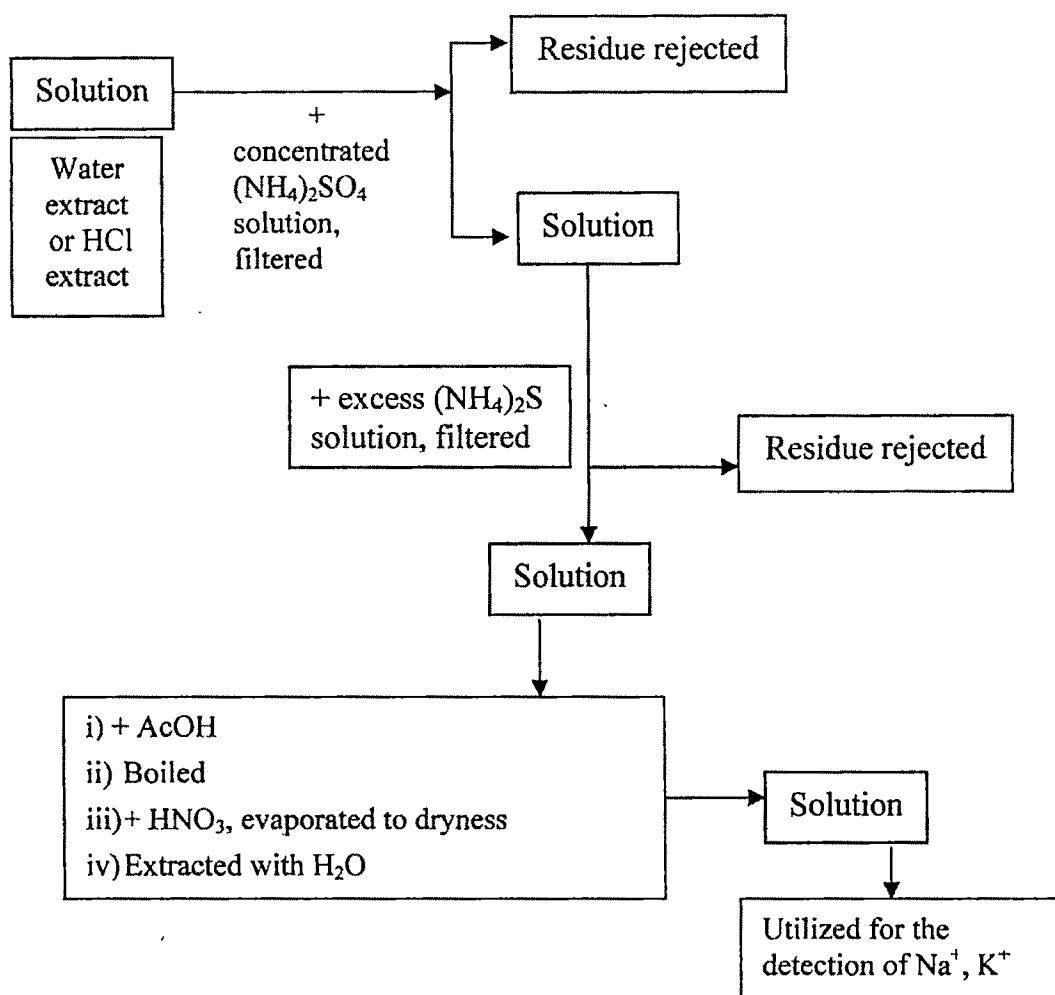
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N.B.

- i) As Ca^{2+} , Sr^{2+} and Ba^{2+} are precipitated as sulfate in acid medium, the anions PO_4^{3-} , BO_3^{3-} and F^- cannot interfere.
- ii) When Mn^{2+} , Ni^{2+} , Fe^{3+} , Co^{2+} , Cu^{2+} are freshly precipitated as phosphate, borate or fluoride can be converted into hydroxide without any difficulty.
- iii) Al^{3+} , Zn^{2+} and Cr^{3+} are detected from the anions $\text{Al}(\text{OH})_4^-$, $\text{Zn}(\text{OH})_4^{2-}$ and CrO_4^{2-} . These are not interfered by PO_4^{3-} , BO_3^{3-} and F^- .

Detection of Na^+ , K^+ :

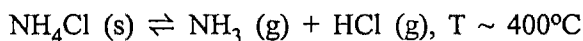


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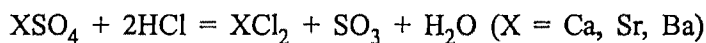
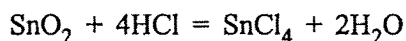
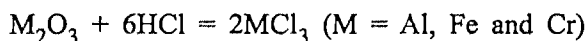
Analysis of Insoluble Materials :

The preliminary tests, viz. (i) flame test (ii) borax bead test and (iii) fluorescence test must be performed with the sample as these will provide valuable information regarding the insoluble material. Thus transient brick red flame is indicative of CaSO_4 , yellow borax bead is indicative of Fe_2O_3 , crimson red flame is indicative of SrSO_4 and CaF_2 and so on.

For wet analysis of cations and anions, the sample may be ignited with solid NH_4Cl when the following reactions will take place :



(At standard pressure, BP of constant boiling $\text{HCl} = 110^\circ\text{C}$)



AlCl_3 , FeCl_3 and SnCl_4 being volatile, during ignition the mouth of the ignition tube should be covered with a filter paper soaked with water. The contents on the filter paper should then be extracted with dil HCl and the extract should be utilized for the tests of Al^{3+} , Fe^{3+} and Sn^{4+} in the usual way. The residue left in the ignition tube should also be extracted with HCl and tested for the detection of the other cations. If CaSO_4 , SrSO_4 , BaSO_4 and CaF_2 are indicated in the dry test then for the tests of SO_4^{2-} and F^- , the mouth of the ignition tube should be covered with filter paper soaked with water. The filter paper should be washed with dil HCl and the solution is utilized for the tests of SO_4^{2-} and F^- .

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Part–II (Year 2)

Quantitative Inorganic Analysis

1. 1 General Discussion :

Chemical analysis is a kind of investigation or operation related to the determination of the components of matter with respect to the qualitative and quantitative aspects. Qualitative analysis aims at determining the identity of elemental or molecular components of matter but the quantitative analysis refers to determine the quantity of the material components.

In quantitative analysis various methods are adopted. The most useful methods are:

- (i) Volumetric or Titrimetric Analysis
- (ii) Gravimetric Analysis
- (iii) Instrumental Analysis

Volumetric or Titrimetric Analysis :

It is a quantitative chemical analysis based upon the measuring of volume of solution of the reactants and following the equivalence point of the stoichiometric reaction. In actual practice, a certain volume of solution of accurately known concentration of one reactant is allowed to react completely by mixing with a fixed volume of a solution of other and then the equivalence point of the stoichiometric reaction is identified with the help of auxiliary reagent known as “indicator”. This process is termed a “titration”. So, the “volumetric analysis” sometimes is termed as “titrimetric analysis”. The solution of accurately known strength is called the “standard solution” (or called “titrant”) and the solution of the substance being titrated is called “titrate”. The solution of unknown strength is then calculated from the titration data by applying the laws of chemical equivalence.

The “equivalence point” or the “theoretical (or stoichiometric) end point” is such a specific point where the chemical reaction is just complete in absolute sense. But in titration process the completion of a chemical reaction is detected practically by the visual change of colour/turbidity of the indicator into the solution and that completion point is called the “end point” of the titration. In the ideal titration the visible end point will coincide with the stoichiometric or theoretical end point. In practice, however, a small difference usually occurs, which represents the “titration error”. We should always try to select an indicator fitting with the experimental conditions such that the difference between the visible end point and the equivalence point is as small as possible.

To enter into volumetric analysis a reaction must fulfill the following condition :

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- (i) The reaction should be simple and specific and must be expressed by a chemical equation. No side reaction will be there. The reactants must react in stoichiometric or equivalent proportions.
- (ii) The reaction should proceed with high speed and should be completed (i.e., 100%).
- (iii) If the reaction is slow, then a catalyst must be there to increase the speed of the reaction.
- (iv) There must be a marked change in some physical or chemical property of the solution at the equivalence point.
- (v) An indicator/instrument should be available which is able to define sharply the end point of the reaction by changing its own physical property like colour, formation of precipitate, pH, electrical potential, conductance etc. in solution.

Classification of reactions in volumetric analysis :

Two main classes are :

- (a) Those in which no change in valence occurs, i.e., ionic reactions.
- (b) Those involve a change of valence, i.e., electron transfer occurs which are called oxidation-reduction reactions.

The above two types of reactions may be classified in other ways as:

- (i) Acidimetry and alkalimetry where acids and bases react
- (ii) Oxidimetry and reductimetry where oxidants and reductants react
- (iii) Complexometry where complex formation reactions take place
- (iv) Argentometry where silver nitrate solution is used to conduct precipitation titration.

Volumetric or titrimetric method offers an accuracy of 1 part in 1000 to perform, less costly and simple apparatus are used. The following are the main requirements for volumetric analysis :

- (i) for the measurement of accurate volume of liquids: burettes, pipettes, measuring flasks, measuring cylinders etc.
- (ii) for the preparation of standard solutions: chemical balance with calibrated weights or a digital balance, some standard chemicals etc.
- (iii) for the detection of equivalence point of the titrations visual indicators or some specific instruments.
- (iv) miscellaneous types of laboratory chemicals and apparatus.

1. 2 Use of solution of the reactants:

To carry out a chemical reaction successfully, intimate mixing of the reactants in molecular/ ionic/atomic levels is highly essential and to have it, solution (or gas) phase of the reacting

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components is preferred because, in such state, components remain in dispersed situation and hence are easier to react.

Any suitable solvent may be used for this purpose. As water is a universal solvent, it is widely used as a common solvent to conduct a chemical reaction in solution in most cases of volumetric analysis.

There are some substances which may be directly dissolved in water. Some others may enter into the solution through selective chemical reactions. The solution thus prepared in water is called water extract. In quantitative analysis the quantity of the reacting components in solution are also important data. Strengths are expressed in various units: (i) Molar unit, (ii) Equivalent unit, (iii) Percentage unit, etc.

- (i) **Molar unit** : Molar unit is expressed in terms of "Molarity" (M) and is defined as the number of gram moles of the solute present in one litre of the solution at room temperature (g mole/lit).

$$\text{Molarity (M)} = \frac{\text{Weight of the solute in grams present in one litre solution}}{\text{Gram molecular weight of the substance}}$$

For example, molecular weight of Na_2CO_3 is 106 and when 159 gram Na_2CO_3 is present in one litre of the solution, it will be $159/106 = 1.5(\text{M})$ solution.

- (ii) **Equivalent unit** : It is expressed in terms of "Normality" (N) and is defined as the number of gram equivalents of the solute present in one litre of the solution. As chemical reactions occur in equivalent weight ratio of the reactants, it is more practical and useful unit in volumetric analysis.

$$\text{Normality (N)} = \frac{\text{Weight of the solute in grams present in one litre solution}}{\text{Gram equivalent weight of the substance}}$$

Let, m grams of the solute is dissolved in a solvent to make V litres of a solution and if E is the gram equivalent weight of the solute, then the strength of the solution in

$$\text{Normality (N)} = \frac{m/V}{E} = \frac{m}{EV}$$

Equivalent weight of NaOH is 40 and if 8 grams of NaOH is present in two litre solution, then its strength in normality = $\frac{8/2}{40}(\text{N}) = 0.1(\text{N})$

- (iii) **Percentage strength**: The number of grams of the solute present in 100 ml of the solution is called the percentage strength (%). 10% NaOH solution means 10 gram NaOH is present in 100 ml of the solution.

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Types of solution : It may be of two types: (i) Primary standard solution (ii) Secondary standard solutions.

- (i) **Primary standard solution :** A solution of exactly known strength of a solute is called a standard solution. The nature of the solute in solution dictates the quality of the standard solution. There are some stable substances which exist in the pure state and that purity remains intact in its environment for a reasonable period of time. e.g. $K_2Cr_2O_7$, $KBrO_3$, Borax, anhydrous Na_2CO_3 etc. If an accurate weight of one of those substances is dissolved in a known volume of the solution, the solution prepared will be a primary standard solution. The accuracy of strength in preparing a primary standard solution is vital in volumetric analysis. To take exact weight of a primary standard substance up to 4th decimal place we may use a sensitive double pan chemical balance and calibrated weights or we may use single pan digital balance of the same standard. The latter is easier and time saver to a user. The strength factor of the solution = accurate weight of a substance taken in gram in a given volume of the solution/weight to be taken in gram.
- (ii) **Secondary standard solution :** Certain substances e.g. HCl , $NaOH$, $KMnO_4$, $Na_2S_2O_3$ etc. always contain a certain degree of impurity. Due to this, accurate weighing is meaningless and thus a solution made by taking a rough weight of them will produce a solution of secondary standard. So the exact strength of a secondary standard solution is determined by performing a titration using suitable primary standard solution as a reactant. The process is known as standardization.

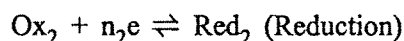
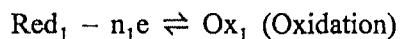
1. 3 The essential features of redox reactions:

One of the important reactions is the redox reaction which occurs in volumetric titrations frequently.

Oxidation means loss of electron(s) and reduction means gain of electron(s). Both the oxidation and reduction processes occur simultaneously. Titration involving a complete oxidation and reduction reaction in solution is called a redox titration.

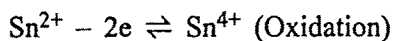
A. Equivalent weights of oxidants and reductants :

According to the definition, oxidation and reduction reactions may be represented as:

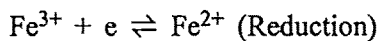


where Red_1 and Red_2 are the different reductants, Ox_1 and Ox_2 different oxidants, n_1 and n_2 are the different number of electrons. During reaction, oxidants get reduced and reductants get oxidized, e.g.

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Reductant Oxidant



Oxidant Reductant

Therefore, in a redox reaction, the equivalent weight (E) of an oxidant is the weight of it that accepts one mole of electrons and the equivalent weight (E) of a reductant is the weight that loses one mole of electrons. And in a redox titration, at the equivalence point, i.e. at the end point of the titration, both the oxidant and reductant complete the chemical reaction to their equivalent weight ratio. In the above reaction, equivalent weight of reductant (Sn^{2+}) = atomic weight/2 = $118.7/2 = 59.35$ and that of oxidant (Fe^{3+}) = atomic weight/1 = $55.85/1 = 55.85$. Therefore, 59.35 parts by weight of Sn^{2+} is equivalent to 55.85 parts by weight of Fe^{3+} in the redox reaction. Equivalent weights of some reacting substances are given in table :

Substances (molecular weight)	Equation of ion-electron change reaction	Equivalent weight (E)* =
$\text{K}_2\text{Cr}_2\text{O}_7$ (294.22)	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	$294.22/6 = 49.037$
KMnO_4 (158)	$\text{MnO}_4^- + 8\text{H}^+ + 5e \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$158/5 = 31.6$
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (278)	$\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$	$278/1 = 278$
$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (392)	$\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$	$392/1 = 392$
$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (126)	$2\text{CO}_2 + 2e \rightarrow \text{C}_2\text{O}_4^{2-}$	$126/2 = 63$
I_2 (254)	$\text{I}_2 + 2e \rightarrow 2\text{I}^-$	$254/2 = 127$
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (248)	$\frac{1}{2}\text{S}_4\text{O}_6^{2-} + e \rightarrow \text{S}_2\text{O}_3^{2-}$	$248/1 = 248$
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (249.69)	$\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$	$249.69/1 = 249.69$
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (225.6)	$\text{Sn}^{4+} + 2e \rightarrow \text{Sn}^{2+}$	$225.6/2 = 112.8$

*Atomic wt. (A) or Molecular wt. (M)/electrons (n) involved in reaction.

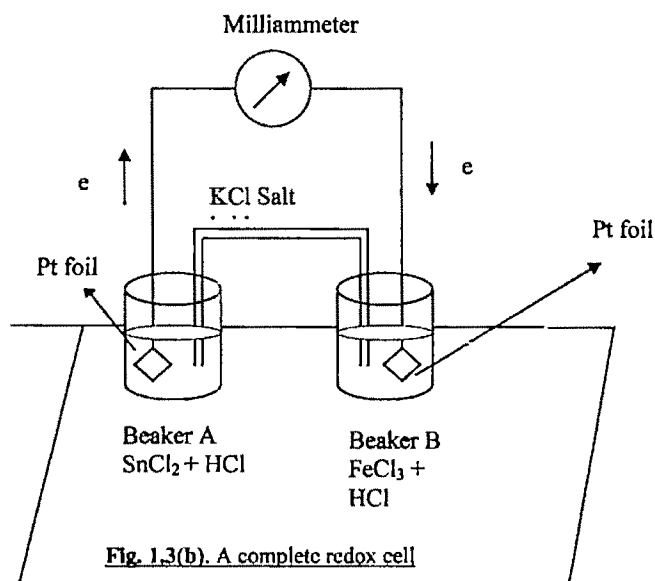
When equivalent weights are expressed in grams these are called gram equivalent weights. When one gram equivalent weight (E) of a substance is dissolved in one litre of the solution, its strength will be 1(N).

B. Oxidation potential and Reduction potential :

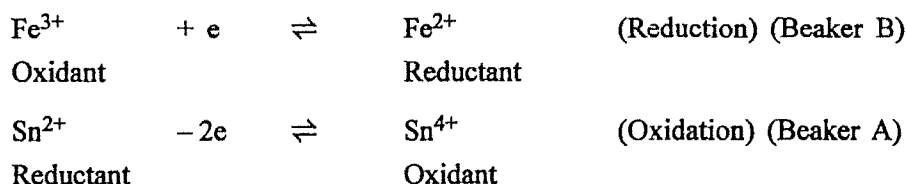
Oxidation involves the loss of electrons, reduction involves the gain of electrons and therefore, electrons flow i.e. electric current flow from the reductants to the oxidants in

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molecular level to neutralize each other in a haphazard way so that no net current flow during a redox reaction. This is the general feature of a redox reaction. But any redox process may be demonstrated by taking the two systems separately as :



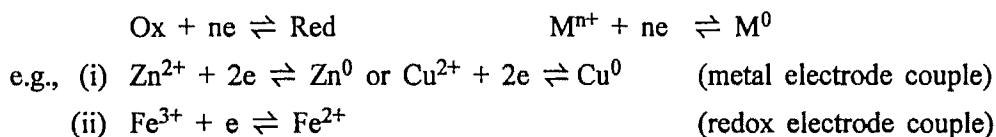
Beaker A contains one mole SnCl_2 in HCl and beaker B contains one mole FeCl_3 in HCl . Two Pt-foils are dipped into the two different solutions and are connected by a wire through a milliammeter. A KCl salt bridge connects the two beakers as shown in Fig. 1.3(b). When the connection is made, electron flow has been detected from beaker A to beaker B with the deflection of needle of milliammeter. After sometime the yellow colour of Fe^{3+} in beaker B has been discharged with the formation of Fe^{2+} and Sn^{4+} has been detected in beaker A. The current flows due to the reactions are:



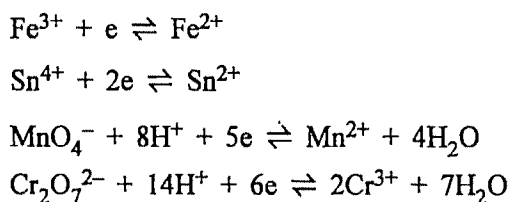
The oxidation process ($\text{Sn}^{2+} - 2e \rightleftharpoons \text{Sn}^{4+}$) enriched the Pt-foil (electrode) with electrons acting as Anode (-) with respect to the solution (Beaker A) and the potential developed is denoted as oxidation potential (E_{Ox}). On the other hand, the reduction process ($\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$) depleted the Pt-foil (electrode) in electrons acting as Cathode (+) with respect to the solution (Beaker B) and the potential developed is denoted as reduction potential (E_{Red}). Further, the current flow indicated by the ammeter is due to the potential difference between the two electrodes (Cathode and Anode) called the cell potential or cell emf (E_{Cell}).

C. Single electrode potential and standard reduction potential :

When a metal is dipped partially into a solution of its salt (called metal electrode, e.g., Zn in ZnSO_4) or when an inert electrode like Pt is partly dipped into a solution of a conjugate oxidant-reductant couple (redox couple) (called redox electrode, e.g., $\text{Fe}^{3+} - \text{Fe}^{2+}$, Pt), an electrical potential difference (E) is developed between the metal plate and the solution. This is due to the following reason: some metal atoms by losing electrons on the metal surface pass into the solution as cations while some metal ions from solution, by taking the electrons from the metal surface, get deposited as metal atoms on the metal surface. Thus, the two opposite process of oxidation and reduction quickly establish a state of equilibrium as:



If the tendency of oxidation is higher than that of reduction then the metal plate will be negatively charged called Anode (–) and the solution phase will get positively charged. On the other hand, if the tendency of reduction is higher, then the charge separation will be just opposite i.e. metal plate will be positively charged called Cathode (+). In case of redox electrodes (a redox couple and an inert metal plate like Pt) the similar state of equilibrium among the oxidants, reductants and electrons in solution are seen to establish for which a similar charge separation between the plate and solution results. Illustrative reaction couples are:



Due to this charge separation between the metal plate and the solution phase, there will be an electrostatic attraction giving rise to an electrical double layer. As a result, a difference of electrical potential between the metal plate and the solution phase will arise and it is described as the single electrode potential of the system $\left(E_{\text{Ox/Red}}^0; E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 \right)$.

Conventionally, the redox reactions are written in terms of reduction reactions like $\text{Ox} + ne \rightleftharpoons \text{Red}$ and the single electrode potential is expressed in terms of single reduction potential (E). It is evaluated by the Nernst equation as:

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{Ox}}}{a_{\text{Red}}}$$

As activity is rather difficult to measure in most cases of quantitative analysis, it remains sufficiently accurate to replace activity (a) by concentration (c), symbol [].

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$$\text{Therefore, } E = E^0 + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

E = Single reduction potential in volt

E^0 = Standard reduction potential in volt.

R = Universal gas constant = 8.314 Joules/Kelvin/mole (Joule = Volt \times Coulomb)

T = Absolute temperature = 298K (at STP)

F = Faraday = 96500 coulomb per mole of electrons

n = Number of electrons involved in redox reaction.

$[\text{Ox}]$ = Concentration of the oxidant, $[\text{Red}]$ = Concentration of the reductant

$$\begin{aligned} E &= E^0 + \frac{8.314 \times 298}{n \times 96500} \times 2.303 \log_{10} \frac{[\text{Ox}]}{[\text{Red}]} \\ &= E^0 + \frac{0.0591}{n} \log_{10} \frac{[\text{Ox}]}{[\text{Red}]} \end{aligned}$$

At STP, when $[\text{Ox}] = [\text{Red}]$, then $E = E^0$ = Standard reduction potential. Thus, standard reduction potential (E^0) is the electromotive force (emf) of a redox system (couple) which is measured under standard conditions (i.e., all type of ions are at unit concentration (1M), metals are solid and gases are measured at one atmospheric pressure and temperature at 25°C. Standard reduction potential is denoted as ($E^0_{\text{Ox/Red}}$ i.e., $E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}}$) and is a significant parameter of the system.

For quantitative study of redox reactions with the use of E^0 value, it is convenient to consider that a solution of an oxidant is always associated with some amount of the conjugate reductant however small. Similarly, the same concept is applied in case of a reductant and so also to all redox couple. That is, a solution of Fe^{3+} is always associated with some Fe^{2+} , however small, so that a $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple exists. Similarly for I_2 solution the $\text{I}_2/2\text{I}^-$ redox couple exists.

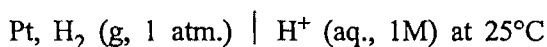
D. Measurement of Electrode Potential and Standard Reduction Potential :

The absolute value of electrode potential of an electrode is not possible to measure. With the help of a suitable reference electrode (whose potential is standard and known), the potential of a unknown redox electrode system is actually measured. For this purpose, a galvanic cell is to be set up by coupling the electrode whose potential is to be measured

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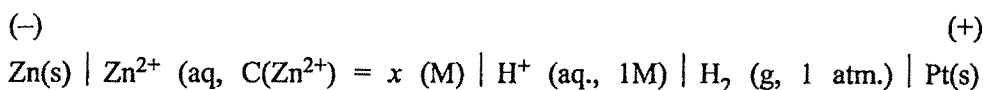
and a specific reference electrode. The measured cell emf is the difference of the electrode potential of the two electrodes coupled. The value of the unknown potential can then be calculated. For this purpose, the standard hydrogen electrode (SHE) is used as standard reference electrode.

A standard hydrogen electrode is constituted by bubbling pure H_2 gas at one atmosphere pressure through one molar HCl ($a_{H^+}=1$) and a platinised Pt-wire is dipped at $25^\circ C$, the potential of which has been arbitrarily and universally fixed at zero (0) volt. It may be described as :



The corresponding half cell reactions are: $H^+(aq) + e \rightleftharpoons \frac{1}{2}H_2 (g)$ and potential is assigned fixed at zero (0) volt $\left(E_{H^+/\frac{1}{2}H_2}^0 = 0.00V \right)$.

Now, to know the unknown potential of an electrode say, the $Zn/ZnSO_4$ electrode, it has to be coupled with SHE just to form a galvanic cell like :



The electromotive force (emf) of the produced cell (E_{Cell}) is the algebraic difference between the electrode potentials of the cathode (+) and the anode (-) (two half cells).

$$\begin{aligned} E_{Cell} &= E_{Cathode} - E_{Anode} = E_{H^+/\frac{1}{2}H_2} - E_{Zn^{2+}/Zn} \\ &= E_{H^+/\frac{1}{2}H_2}^0 - E_{Zn^{2+}/Zn} \\ &= 0.00 - E_{Zn^{2+}/Zn} \\ &= -E_{Zn^{2+}/Zn} \text{ Volt} \end{aligned}$$

(Since, at STP, $E_{H^+/\frac{1}{2}H_2} = E_{H^+/\frac{1}{2}H_2}^0 = 0.00 \text{ Volt}$)

So, the measured cell potential i.e., the single electrode potential or single reduction potential of $Zn/ZnSO_4$ electrode system is $E_{Cell} = -E_{Zn^{2+}/Zn}$ Volt. But, if Zn metal is dipped into one mole per litre of $ZnSO_4$ solution [i.e., $C_{Zn^{2+}} = x (M) = 1(M)$] at $25^\circ C$, then the cell that would form a standard one and at that case $E_{Cell}^0 = -E_{Zn^{2+}/Zn}^0 = -0.76 \text{ Volt}$. (experimentally observed value). Therefore, the standard reduction potential of Zn^{2+}/Zn system is $E_{Zn^{2+}/Zn}^0 = -0.76 \text{ Volt}$.

Similarly, in case of $Cu/CuSO_4$ ($x \text{ mol/lit}$) vs. SHE, the following galvanic cell is formed: $Pt(s) \mid H_2(g, 1atm) \mid H^+(aq, 1M) \mid Cu^{2+}(aq, xM) \mid Cu(s)$ for which

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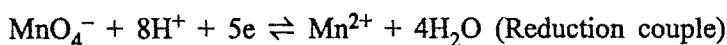
$$\begin{aligned}
 E_{\text{Cell}} &= E_{\text{Cathode}} - E_{\text{Anode}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{H}^+/\frac{1}{2}\text{H}_2} \\
 &= E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{H}^+/\frac{1}{2}\text{H}_2}^0 = E_{\text{Cu}^{2+}/\text{Cu}} - 0 \\
 &= E_{\text{Cu}^{2+}/\text{Cu}} \left(\text{as } E_{\text{H}^+/\frac{1}{2}\text{H}_2}^0 = 0 \right)
 \end{aligned}$$

At standard state ($C_{\text{Cu}^{2+}} = 1\text{M}$) and at 25°C), the standard reduction potential of the Cu^{2+}/Cu system will be equal to standard cell potential (E_{Cell}^0) i.e.,

$$E_{\text{Cell}}^0 = E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34\text{V (measured value).}$$

Thus, the reduction potential of any redox systems such as $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Sn}^{4+}/\text{Sn}^{2+}$, MnO_4^- , $\text{H}^+/\text{Mn}^{2+}$, $\text{Cr}_2\text{O}_7^{2-}$, $\text{H}^+/\text{Cr}^{3+}$ etc. may be measured at any situation (standardised or unstandardised) in the same way like metal electrodes system as above.

Measurement of cell potential (E_{Cell}) of any two separate redox systems may also be determined by coupling the two systems to form a complete cell like galvanic cell. As for example, $\text{Fe}^{3+}/\text{Fe}^{2+}$ and MnO_4^- , $\text{H}^+/\text{Mn}^{2+}$ system (say) Fig. 1.3(d),



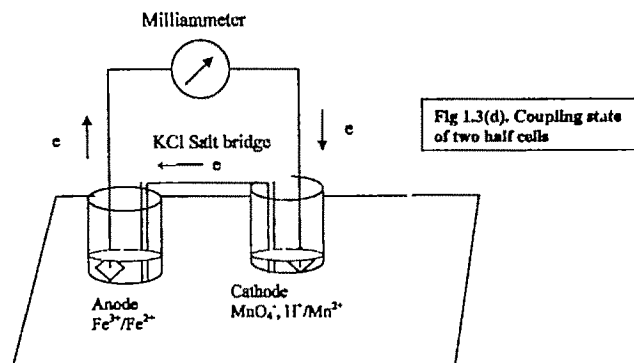
$$E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$$

$$= \left(E_{\text{MnO}_4^-, \text{H}^+/\text{Mn}^{2+}}^0 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]} \right) - \left(E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 + \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right)$$

$$= \left(E_{\text{MnO}_4^-, \text{H}^+/\text{Mn}^{2+}}^0 - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 \right) + \left(\frac{0.0591}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]} - \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right)$$

$$= \left(E_{\text{MnO}_4^-, \text{H}^+/\text{Mn}^{2+}}^0 - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 \right) + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8[\text{Fe}^{2+}]^5}{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}$$

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Therefore, E_{cell} depends mainly on the concentration terms of the components involved in redox reaction. At the standard state, i.e., $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 1(\text{M})$; $[\text{MnO}_4^-] = [\text{Mn}^{2+}] = 1(\text{M})$; $[\text{H}^+] = 1(\text{M})$, then at 25°C .

$$E_{\text{Cell}} = \left(E_{\text{MnO}_4^-, \text{H}^+/\text{Mn}^{2+}}^0 - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 \right) \text{ Volt} = (1.51 - 0.77) \text{ Volt} = 0.74 \text{ Volt}.$$

The standard H-electrode is rather difficult to manipulate. So other suitable electrode like the calomel electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2(\text{s}), \text{KCl}(\text{sol.})$), the cell reaction is $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$ or the silver-silver chloride electrode whose potential is known and standardized with respect to SHE, can be used to construct the galvanic cells and to evaluate the potentials of unknown electrodes.

A list of measured standard reduction potential values of some redox systems are given below :

Electrode reaction	$E^0(\text{Volt})$
$\text{F}_2 + 2\text{e}^- \rightleftharpoons 2\text{F}^-$	+2.85
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}$	+2.01
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.51
$\text{BrO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightleftharpoons \frac{1}{2}\text{Br}_2 + 3\text{H}_2\text{O}$	+1.52
$\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+}$	+1.44
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{IO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightleftharpoons \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}$	+1.20
$\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	+1.07

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$2\text{Hg}^{2+} + 2e \rightleftharpoons \text{Hg}_2^{2+}$	+0.92
$\text{Cu}^{2+} + \text{I}^- + e \rightleftharpoons \text{CuI}$	+0.86
$\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightleftharpoons 4\text{OH}^-$	+0.82
$\text{Hg}_2^{2+} + 2e \rightleftharpoons 2\text{Hg}$	+0.79
$\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3e \rightleftharpoons \text{MnO}_2 + 4\text{OH}^-$	+0.59
$\text{AsO}_4^{3-} + 2\text{H}^+ + 2e \rightleftharpoons \text{AsO}_3^{3-} + \text{H}_2\text{O}$	+0.56
$\text{I}_2 + 2e \rightleftharpoons 2\text{I}^-$	+0.54
$[\text{Fe}(\text{CN})_6]^{3-} + e \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	+0.36
$\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$	+0.35
$\text{Cu}^+ + e \rightleftharpoons \text{Cu}$	+0.15
$\text{Sn}^{4+} + 2e \rightleftharpoons \text{Sn}^{2+}$	+0.15
$\text{S}_4\text{O}_6^{2-} + 2e \rightleftharpoons 2\text{S}_2\text{O}_3^{2-}$	+0.08
$2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$	0.000
$\text{Pb}^{2+} + 2e \rightleftharpoons \text{Pb}$	-0.13
$\text{Sn}^{2+} + 2e \rightleftharpoons \text{Sn}$	-0.14
$\text{Cr}^{3+} + e \rightleftharpoons \text{Cr}^{2+}$	-0.41
$\text{Fe}^{2+} + 2e \rightleftharpoons \text{Fe}$	-0.44
$2\text{CO}_2 + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4$	-0.45
$\text{Fe}(\text{OH})_3 + e \rightleftharpoons \text{Fe}(\text{OH})_2 + \text{OH}^-$	-0.56
$\text{AsO}_4^{3-} + 3\text{H}_2\text{O} + 2e \rightleftharpoons \text{H}_2\text{AsO}_3^- + 4\text{OH}^-$	-0.67
$\text{Zn}^{2+} + 2e \rightleftharpoons \text{Zn}$	-0.76
$\text{Al}^{3+} + 3e \rightleftharpoons \text{Al}$	-1.66
$\text{Na}^+ + e \rightleftharpoons \text{Na}$	-2.71

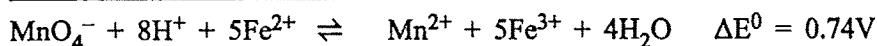
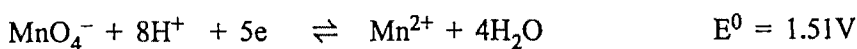
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The table shows that: (a) the redox couples with positive E^0 values occupy a position above ($2H^+/H_2$ system, $E^0 = 0.00$ Volt) and those with negative E^0 values occupy a position below it.

(b) Oxidant components of the redox couples of higher positive value of standard reduction potential are powerful oxidising agent and the reductant components of the redox couples with higher negative standard reduction potentials are powerful reducing agents.

(c) Oxidant component of a redox couple occurring upper in the table may oxidize the reductant component of a redox couple occurring lower in the table of standard reduction potentials, provided the difference between the E^0 values of the couples is appreciable (approximately $\Delta E^0 > 0.15V$).

E^0 values show that MnO_4^- is a powerful oxidant (for higher E^0 value) in acid medium and it will oxidize Fe^{2+} to Fe^{3+} . Reactions are :



Since $\Delta E^0 = +ve$, and standard free energy change $\Delta G^0 = -nFE^0 = -ve$, the reaction is spontaneous. So Fe^{2+} can be estimated by titration with a standard solution of $KMnO_4$ in 2(N) H_2SO_4 medium. Based upon this concept redox volumetric titrations may be chosen to carry out for the estimation of oxidants or reductants in laboratory.

E. Formal Potentials of Redox Systems

For a single electrode process, $Ox + ne \rightleftharpoons Red$, the potential is given by the equation

$$E = E^0 + \frac{0.0591}{n} \log \frac{a_{Ox}}{a_{Red}} \text{ at } 25^\circ C$$

But when $a_{ox} = a_{red} = 1$ (unit activity), then $E = E^0$ and it is called standard reduction potential. In solution, activity (a) = molar concentration (c) \times activity coefficient (f). In dilute solution activity coefficient (f) approaches unity and activity approaches concentration i.e., $a = c$, when $f = 1$. In actual practice, concentration but not activity of the reactants are used and further, not a dilute solution but a concentrated solution of the reactants are taken up in experiments. On the other hand, concerned ions may not exist in simple forms in the presence of other ions in real case. Under these circumstances, the activity (a) and concentration (c) of the involved components differ much. So, the concept of standard potential has no practical use in real situation and is therefore replaced by more appropriate term "formal potential". The experimentally determined potential (i.e., effective potential) of a redox system having one molar concentration of each of oxidant and reductant which covers all other adverse effects (such

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as concentration effect, pH effect, precipitation, complex formation effect etc.) in solution is called formal potential (E^f). Nernst equation in those cases is

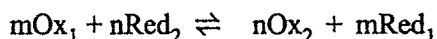
$$E = E^f + \frac{0.0591}{n} \log \frac{[\text{Ox}]}{[\text{Red}]} \text{ at } 25^\circ\text{C}$$

The value of electrode potential (E) is solely determined by the ratio $[\text{Ox}]/[\text{Red}]$ and when the ratio $[\text{Ox}]/[\text{Red}] = 1$, then $E = E^f =$ formal potential.

As for example, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system in 1(M) HCl exists in different forms like $\text{Fe}(\text{OH})^{2+}$, FeCl_2^+ , FeCl_4^- , $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ etc. The value of E^f decreases as complexation of Fe^{3+} increases. When $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.77\text{V}$, the $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^f$ of the same system in 1(M) HCl is 0.70V and 0.61V in 1 (M) H_2SO_4 + 0.5 (M) H_3PO_4 mixture.

F. Cell Potential and Equilibrium Constant of a Redox Reaction :

A complete redox reaction may be assumed to happen in a galvanic cell and the overall redox reaction at the state of equilibrium may be represented in general, as :



The equilibrium constant (K) of the overall redox reaction may be defined as

$$K = \frac{[\text{Ox}_2]^n [\text{Red}_1]^m}{[\text{Ox}_1]^m [\text{Red}_2]^n}$$

The half cell reactions that occur under the above overall reaction may be written as:



and the potentials of the two processes are:

$$E_1 = E_1^f + \frac{0.0591}{n} \log \frac{[\text{Ox}_1]}{[\text{Red}_1]}$$

$$E_2 = E_2^f + \frac{0.0591}{m} \log \frac{[\text{Ox}_2]}{[\text{Red}_2]}$$

At the state of equilibrium and also at the equivalence point, the electrode potentials of the two different systems (two half cells) become equal; i.e. $E_1 = E_2$. Therefore,

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$$E_1^f + \frac{0.0591}{n} \log \frac{[\text{Ox}_1]}{[\text{Red}_1]} = E_2^f + \frac{0.0591}{m} \log \frac{[\text{Ox}_2]}{[\text{Red}_2]}$$

Multiplying both sides of the equation by mn and simplifying

$$mn(E_1^f - E_2^f) = 0.0591 \log \frac{[\text{Ox}_2]^n [\text{Red}_1]^m}{[\text{Ox}_1]^m [\text{Red}_2]^n} = 0.0591 \log K$$

$$\log K = \frac{mn(E_1^f - E_2^f)}{0.0591}$$

$$K = 10^{\frac{mn(E_1^f - E_2^f)}{0.0591}}$$

$$= 10^{\frac{mn\Delta E^f}{0.0591}}$$

For a simple redox system with $m = n = 1$, the value of equilibrium constant (K) is

$$K = 10^{\frac{(E_1^f - E_2^f)}{0.0591}}$$

$$= 10^{\frac{\Delta E^f}{0.0591}}$$

where $\Delta E^f = E_1^f - E_2^f = \text{Cell potential (or cell emf)}$.

For the reaction $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightleftharpoons \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$ ($n = 5$, $m = 1$)

$$K = 10^{\frac{1 \times 5 \left(E_{\text{MnO}_4^-/\text{Mn}^{2+}}^f - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^f \right)}{0.0591}}$$

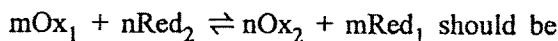
$$= 10^{\frac{1 \times 5 (1.51 - 0.77)}{0.0591}}$$

$$= 10^{62}$$

Since the value of equilibrium constant (K) is very high, the reaction is feasible and will be completed quantitatively.

G. Condition for Completion of a Redox Reaction :

A redox reaction is said to be complete when it is 99.9%. In this situation the equilibrium constant (K) of the general redox reaction like



$$\begin{aligned} K_{\min} &= \frac{[\text{Ox}_2]^n [\text{Red}_1]^m}{[\text{Ox}_1]^m [\text{Red}_2]^n} = \left\{ \frac{[\text{Ox}_2]}{[\text{Red}_2]} \right\}^n \left\{ \frac{[\text{Red}_1]}{[\text{Ox}_1]} \right\}^m \\ &= \left\{ \frac{99.9}{0.1} \right\}^n \left\{ \frac{99.9}{0.1} \right\}^m \\ &\approx 1000^n \times 1000^m = 10^{3(m+n)} \end{aligned}$$

$$\text{We know, } K = 10^{\frac{mn(E_1^f - E_2^f)}{0.0591}}$$

$$\therefore \frac{mn(E_1^f - E_2^f)}{0.0591} = 3(m+n)$$

$$\text{or, } (E_1^f - E_2^f)_{\min} = \Delta E^f = \frac{0.0591 \times 3(m+n)}{mn}$$

Thus, under the above condition a redox reaction may be assumed to be complete (i.e. about 99.9%).

For a simple system like $m = n = 1$,

$$\Delta E^f = (E_1^f - E_2^f)_{\min} = \frac{0.0591 \times 3 \times 2}{1 \times 1} = 0.354 \text{ V}$$

But for a system like $m = 1, n = 5$,

$$\Delta E^f = (E_1^f - E_2^f)_{\min} = \frac{0.0591 \times 3(5+1)}{5 \times 1} = 0.2127 \text{ V}$$

The knowledge of electrode potential value of redox systems only explains the feasibility and the extent of reaction from thermodynamic stand point, but not the kinetic aspect such as speed, activation energy etc. of the reaction which are also important for the completion of the reaction within a reasonable time of a titration process. For example, the E^0 of $\text{ClO}_4^-/\text{Cl}^-$ (1.41V) is

higher than that of $\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}$ (1.33V) for the oxidation of Fe^{2+} to Fe^{3+} ($E^\circ = 0.77\text{V}$). But due to high energy requiring “Cl-O” bond breaking process (which is the rate determining step), the activation energy of ClO_4^- as oxidant is very high and as a result the reaction of ClO_4^- vs Fe^{2+} is too slow to carry out with respect to $\text{Cr}_2\text{O}_7^{2-}$ vs Fe^{2+} reaction system in the volumetric analysis. Similarly, due to high energy barrier of reduction of O_2 to O^{2-} ($E^\circ = 1.23\text{V}$) in 1 (M) acid medium by Fe^{2+} , the reaction is extremely slow although equilibrium constant (K) value is large. For this reason Fe^{2+} salts (i.e. Mohr’s salt) in acid medium are stable and may be kept for a certain period of time in laboratory without any noticeable change in its concentration. Even a Mohr’s salt solution can be used as primary standard with reasonable satisfaction.

H. Factors Affecting the Reduction Potential (E) :

The redox potential (E) of a redox system is evaluated by the Nernst equation as :

$$E = E^0 + \frac{0.0591}{n} \log \frac{[\text{Ox}]}{[\text{Red}]} \text{ at } 25^\circ\text{C}$$

The E values of different systems that are obtained from the experiments depend on so many factors. Some of which are discussed with examples.

(a) Effect of concentration : The change of concentration of the oxidants and reductants that are directly involved in Nernst equation alters the value of E to a considerable extent. As for example, in $\text{Fe}^{3+}/\text{Fe}^{2+}$ system ($\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$),

$$E = E^0 + \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = 0.77 + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

When the concentration of Fe^{3+} is 10 times greater than that of Fe^{2+} , the value of E is increased by 0.059 volt. When $[\text{Fe}^{3+}] = 1 \text{ mole/lit}$ and $[\text{Fe}^{2+}] = 0.0001 \text{ mole/lit}$, then

$$E = 0.77 + 0.0591 \log 1/10^{-4} = 1.006 \text{ Volt.}$$

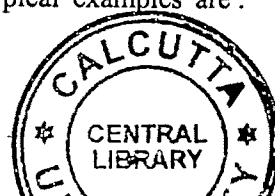
But when $[\text{Fe}^{3+}] = 0.0001 \text{ mole/lit}$ and $[\text{Fe}^{2+}] = 1 \text{ mole/lit}$, the

$$E = 0.77 + 0.0591 \log 10^{-4}/1 = 0.534 \text{ Volt.}$$

Thus, increase in concentration of oxidant increases the value of E and decrease in concentration of oxidant reduces the value of E. Reverse is true for the reductant. Thus power of an oxidant or a reductant is influenced by concentration.

(b) Effect of pH : When $[\text{H}^+]$ or $[\text{OH}^-]$ is directly involved in redox reaction, the value of E is markedly influenced by the pH of the redox reaction media. Typical examples are :

(i) In acid medium (H^+), KMnO_4 acts as a good oxidant.



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The redox reaction is $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$ and

$$E = E^0 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]} \text{ at } 25^\circ\text{C}$$

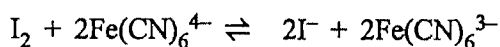
$$E = E^0 + \frac{0.0591}{5} \log [\text{H}^+]^8 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

$$E = E^0 - 0.094\text{pH} + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

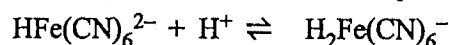
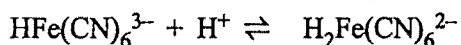
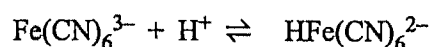
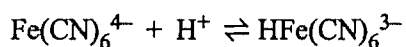
$$= 1.51 - 0.094\text{pH} + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

At pH = 6, the effective reduction potential ($E^0 = 0.946\text{V}$) which falls below both $\text{Cl}_2/2\text{Cl}^-$ ($E^0 = 1.36\text{V}$) and $\text{Br}_2/2\text{Br}^-$ ($E^0 = 1.07\text{V}$) systems and the MnO_4^- oxidizes only I^- to I_2 ($E^0 = 0.54\text{V}$). At pH = 3, the reduction potential of $\text{MnO}_4^-/\text{Mn}^{2+}$ system shifts to 1.23V, then Br^- and I^- both are oxidized except Cl^- . And below pH = 1 its effective reduction potential $E > 1.4\text{V}$, then all I^- , Br^- and Cl^- are oxidized.

(ii) The standard reduction potential of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ and $\text{I}_2/2\text{I}^-$ systems are 0.36 V and 0.54 V, respectively. So, I_2 is able to oxidize $\text{Fe}(\text{CN})_6^{4-}$ to $\text{Fe}(\text{CN})_6^{3-}$ and itself get reduced to I^- as in the reaction:



The equilibrium is to be shifted to right normally at neutral medium. But in sufficiently acidic media, both $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ undergo protonation giving rise to hydroferrocyanic and hydroferricyanic acid species, respectively as:



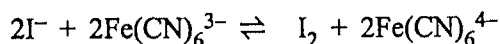
and so on

and so on

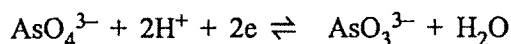
Due to greater negative charge $\text{Fe}(\text{CN})_6^{4-}$ acts as a stronger base, so their respective hydroferrocyno complexes are stabler and less proton releasing with respect to the hydroferricyano complex species in solution equilibria. Therefore, the resultant effective concentration of $\text{Fe}(\text{CN})_6^{4-}$ in acid medium will be diminished considerably with the increase of reduction potential value of the redox system. But E^0 value of $\text{I}_2/2\text{I}^-$ system remains almost same in such acid media. In fact in 1(M) HCl, the observed reduction potential of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$

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system is about 0.71 volt which exceed the reduction potential of $I_2/2I^-$ system. Thus, in strong acid, media, $Fe(CN)_6^{3-}$ practically oxidizes I^- to I_2 quantitatively as :



A similar case of pH dependent reaction is the oxidation of I^- to I_2 by AsO_4^{3-} in acid medium. The reaction is $AsO_4^{3-} + 2H^+ + 2I^- \rightleftharpoons AsO_3^{3-} + H_2O + I_2$, where the standard reduction potentials are given by $E^0 (AsO_4^{3-}/AsO_3^{3-}) = 0.56V$ and $E^0(I_2/2I^-) = 0.54V$, respectively. The couple may be shown as below:

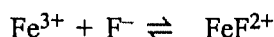


$$E = E^0 + \frac{0.0591}{2} \log \frac{[AsO_4^{3-}][H^+]^2}{[AsO_3^{3-}]} \text{ at } 25^\circ C$$

$$E = E^0 - 0.059 \text{ pH} + \frac{0.0591}{2} \log \frac{[AsO_4^{3-}]}{[AsO_3^{3-}]}$$

At pH = 8 (in $NaHCO_3$ solution) the effective reduction potential becomes about 0.09 V which is less than that of $I_2/2I^-$ system and therefore the reaction proceeds in the reverse direction quantitatively. pH dependence of redox potential is practically important in the redox couple involving oxocations or oxoanions where the oxidant and the reductant components contain different number of oxygen atoms.

(c) Effect of Complex formation: There are many complexing ligands such as NH_3 , CN^- , F^- , PO_4^{3-} , $C_2O_4^{2-}$, bipy, EDTA etc. that may effectively form complexes having higher degree of stability constant (K) with one component with respect to other in a redox couple. Such as F^- , PO_4^{3-} form more stable complex with Fe^{3+} than Fe^{2+} .



$$K = \frac{[FeF^{2+}]}{[Fe^{3+}][F^-]} = 10^5$$

Now the reduction potential of Fe^{3+}/Fe^{2+} system,

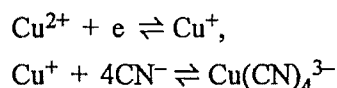
$$E = E^0 + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \text{ at } 25^\circ C$$

$$E = E^0 + 0.0591 \log \frac{[FeF^{2+}]}{K[Fe^{2+}][F^-]}$$

$$= 0.77 + 0.0591 \log 1/10^5 + 0.0591 \log \frac{[\text{FeF}^{2+}]}{[\text{Fe}^{2+}][\text{F}^-]}$$

$$= 0.475 + 0.0591 \log \frac{[\text{FeF}^{2+}]}{[\text{Fe}^{2+}][\text{F}^-]}$$

As the formal reduction potential decreases with increasing F^- concentration, the oxidizing power of Fe^{3+} decreases and it can no more oxidize I^- to I_2 as effective reduction potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ falls below 0.54V ($E_{\text{I}_2/2\text{I}^-}^0$), although normally Fe^{3+} ($E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.77\text{V}$) oxidizes I^- to I_2 in solution. A similar case is seen in the reaction of $\text{Zn} + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}$, where ($E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76\text{V}$) and $E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34\text{V}$. But, in presence of excess CN^- , highly stable $\text{Cu}(\text{CN})_4^{3-}$ ($K = 10^{30}$) is formed :



for which the concentration of Cu^{2+} is diminished to such an extent that the formal reduction potential of Cu^{2+}/Cu system falls below the Zn^{2+}/Zn system.

As a result, $\text{Cu} + \text{Zn}^{2+} \rightleftharpoons \text{Cu}^{2+} + \text{Zn}$ occur in solution. The change of reduction potential through complex formation is highly helpful and selective to estimate one component in presence of others in a mixture without any error of estimation and is frequently used in redox volumetric analysis.

(d) Effect of precipitation : Similarly, precipitation of either component of a redox couple changes concentration of redox species in solution and hence influences the potential of the couple. Some of the important examples are:

(i) Estimation of Cu^{2+} by iodometric method :

The $E_{\text{Cu}^{2+}/\text{Cu}^+}^0 = 0.15\text{V}$ and $E_{\text{I}_2/2\text{I}^-}^0 = 0.54\text{V}$ indicate that Cu^{2+} is unable to oxidize I^- to I_2 due to lower reduction potential value. But in presence of I^- , sparingly soluble CuI precipitate is formed that lowers the concentration of reductant component (Cu^+) of $\text{Cu}^{2+}/\text{Cu}^+$ couple. As a result, the effective reduction potential of $\text{Cu}^{2+}/\text{Cu}^+$ increases over 0.54V of counter I_2/I^- system. So, quantitative oxidation of I^- to I_2 by Cu^{2+} and hence estimation of Cu^{2+} by volumetric method is possible.

$$\text{Cu}^{2+} + \text{e} \rightleftharpoons \text{Cu}^+$$

$$E = E^0 + 0.0591 \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]} \text{ at } 25^\circ\text{C}$$

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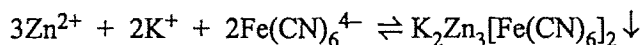
In presence of I^- , Cu^+ is precipitated as CuI , $Cu^+ + I^- \rightleftharpoons CuI \downarrow$. $K_{sp} = [Cu^+][I^-] = 10^{-12}$. (K_{sp} = solubility product).

$$\begin{aligned} \text{So, } E &= E^0 + 0.0591 \log \frac{[Cu^{2+}][I^-]}{K_{sp}} \\ &= 0.15 + 0.0591 \log 10^{12} + 0.0591 \log [Cu^{2+}][I^-] \\ &= 0.86 + 0.0591 \log [Cu^{2+}][I^-] \end{aligned}$$

The formal reduction potential is thus higher over the reduction potential of $I_2 / 2I^-$ system. Therefore, the reaction $2Cu^{2+} + 4I^- = 2CuI + I_2$ occurs quantitatively with I_2 liberation and hence estimation of Cu^{2+} is fruitful.

(ii) Estimation of Zn^{2+} or $Fe(CN)_6^{3-}$ iodometrically :

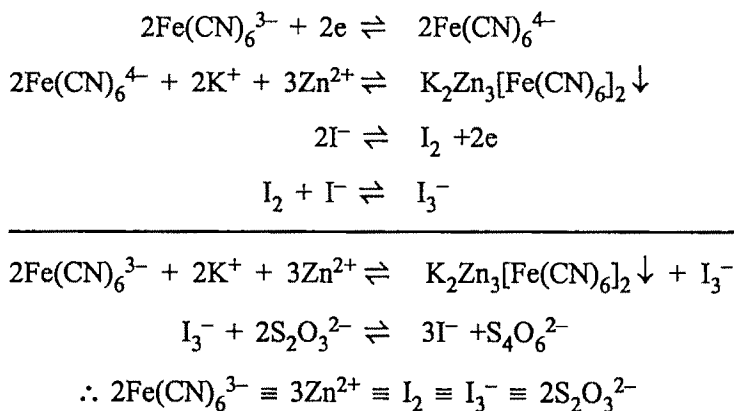
The E^0 of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ is 0.36V and E^0 of $I_2 / 2I^-$ is 0.54 V. So $Fe(CN)_6^{3-}$ should not oxidize I^- . But in presence of Zn^{2+} and K^+ ions, ferrocyanide ion effectively reacts to form stable $K_2Zn_3[Fe(CN)_6]_2$ as precipitate.



As the concentration of reductant component of $Fe(CN)_6^{3-} / Fe(CN)_6^{4-}$ couple decreases, the effective reduction potential of the system

$$E = E^0 + 0.0591 \log \frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]}$$

is thus increased and as a result its oxidizing power is increased. In fact $Fe(CN)_6^{3-}$ oxidizes quantitatively I^- to I_2 in presence of excess Zn^{2+} and K^+ ions in solution and offers a method of estimation of Zn^{2+} and also $Fe(CN)_6^{3-}$ iodometrically using standard thiosulphate solution. The total reactions are:



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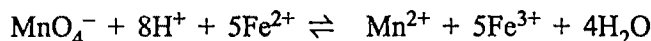
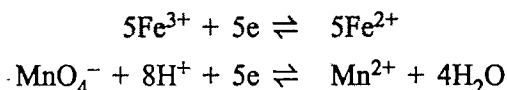
I. Redox Profile in Course of Titration :

In course of titration the amount of oxidant/reductant of the reacting system changes continuously and so also the potential. The plot of change of concentration vs. the corresponding potentials of the system during titration offers the redox profile of the titration.

As a typical example, the titration of 100ml 0.1(M) FeSO_4 solution (titrate) by 0.1(M) KMnO_4 (titrant) in H_2SO_4 having 1(M) H^+ medium is considered. Before the addition of MnO_4^- , the solution in the conical flask contains only Fe^{2+} ions of 0.1(M) in H^+ ions 1(M). The reduction potential (E) of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple is given by

$$E = E^0 + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \text{ at } 25^\circ \text{C}$$

The potential (E) is of course very small at the start as Fe^{3+} is trace (mass action effect). When a few drops of MnO_4^- have been added to Fe^{2+} solution from the burette two redox systems appear and interact to establish an equilibrium as:



In the redox reaction oxidant MnO_4^- destroys Fe^{2+} to produce Fe^{3+} . So, the concentration ratio $[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$ increases and the reduction potential (E) of the resultant solution increases. For the sake of convenience, $\text{Fe}^{3+} / \text{Fe}^{2+}$ couple is considered for calculation of E before equivalence point.

$$E = E^0 + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \text{ at } 25^\circ \text{C}$$

When 50 ml MnO_4^- is added, then $[\text{Fe}^{3+}] / [\text{Fe}^{2+}] = 50/50 = 1$, then $E = E^0 = 0.77 \text{ V}$. The potential of the resultant solution at any point of titration before the equivalence point may be easily calculated by the same way as above. When 90 ml MnO_4^- solution has been added, the potential of the solution is,

$$E = E^0 + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = 0.77 + 0.0591 \log \frac{90}{10} = 0.83 \text{ V}$$

When 99.9 ml MnO_4^- solution is added, then the potential

$$E = 0.77 + 0.0591 \log \frac{99.9}{0.1} = 0.95 \text{ V}$$

When exactly 100.0 ml MnO_4^- solution has been added, then equivalence point is reached.

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At that situation the $\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$ and at equilibrium the potential of both electrode is equal (E_{eq}) and may be written as

$$E_{\text{eq}} = E = 0.77 + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \text{ and}$$

$$E_{\text{eq}} = 1.51 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \quad ([\text{H}^+] = 1 \text{ mol/lit})$$

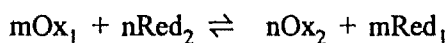
$$\text{or, } 5E_{\text{eq}} = 5 \times 1.51 + 0.0591 \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

Adding the two equations,

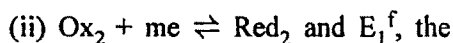
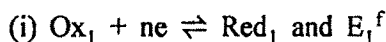
$$\begin{aligned} 6E_{\text{eq}} &= 0.77 + 5 \times 1.51 + 0.0591 \log \frac{[\text{Fe}^{3+}][\text{MnO}_4^-]}{[\text{Fe}^{2+}][\text{Mn}^{2+}]} \\ &= 0.77 + 5 \times 1.51 \text{ (as } [\text{Fe}^{3+}][\text{MnO}_4^-] = [\text{Fe}^{2+}][\text{Mn}^{2+}] \text{)} = 8.32 \text{ V.} \\ \therefore E_{\text{eq}} &= 1.39 \text{ V} \end{aligned}$$

The overall potential of the titrating systems at the equivalence point is called the equivalence potential (E_{eq}) which may be calculated as follows:

For the overall reaction at the equivalence point of



having half cell reactions and potentials



$$E_{\text{eq}} = \frac{mE_1^f - nE_2^f}{m + n}$$

But when an excess MnO_4^- i.e., 100.1 ml has been added, the potential of the electrode may be conveniently calculated by the $\text{MnO}_4^-/\text{Mn}^{2+}$ system.

$$\text{So, } E = E^0 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \quad [\text{at } 1.0 \text{ (M) } \text{H}^+]$$

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$$E = 1.51 + \frac{0.0591}{5} \log \frac{0.1}{100} = 1.47 \text{ V}$$

When 101.0 ml MnO_4^- has been added, the potential

$$E = 1.51 + \frac{0.0591}{5} \log \frac{1}{100} = 1.49 \text{ V}$$

The result of the above computation may be listed in a table below:

No.	KMnO_4 added (ml)	$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$	$\frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$	Value of E(V)
1.	50.0	50:50	—	0.77
2.	90.0	90:10	—	0.83
3.	99.0	99:1	—	0.89
4.	99.9	99.9:1	—	0.95
5.	100.0	—	—	1.39
6.	100.1	—	0.1:100	1.47
7.	101.0	—	1:100	1.49
8.	110.0	—	10:100	1.50

When the potential values at different stages of titration are plotted against the volume of MnO_4^- solution added, a curve like the following is obtained.

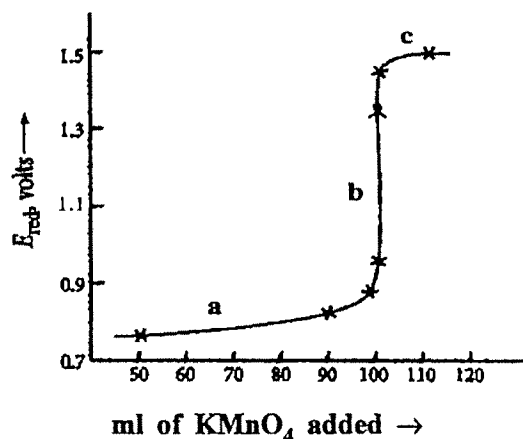
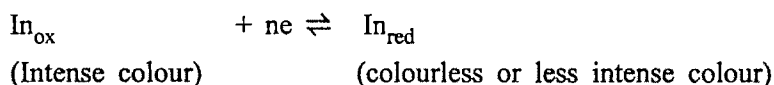


Fig 1.3(i) MnO_4^- vs. Fe^{2+} titration curve

The titration curve Fig 1.3(i) has three different segments: (a) before the equivalence point; (b) at the equivalence; (c) beyond the equivalence point. The speciality of the curve is the sudden rise of potential from 0.95 V (for 99.9% oxidation of Fe^{2+}) up to 1.47 V (for addition of only 0.1 ml of excess KMnO_4 solution). Such abrupt change in potential at the equivalence point (E) [segment (b)] will be seen in all redox titrations and the extent of this abruptness depends on the respective standard potentials of the oxidant and reductant systems. Complex formation, precipitation, pH etc. may alter the concentration of one component with respect to the other of a redox couple and so also the potential of the system. Therefore, the corresponding titration curve changes its nature and shape relative to the ideal one.

J. Use of Indicator in Redox Titration

To identify the equivalence point exactly of a volumetric titration is vital. It may be done visually by observing the sharp change of colour at the equivalence point where one distinct colour of the solution just before the equivalence point changes by the other colour after that point. Instrumental methods may be adopted to locate the equivalence point. But as in redox titration the reduction potential of the redox electrode changes abruptly by large values at the equivalence point, the electrical potential sensitive auxiliary materials may be used for detection of equivalence point. Such auxiliary materials are called redox indicators which are mostly organic dyes and which being present in titrating mixture can undergo change reversible oxidation or reduction due to change of potential of the titration medium imparting different colours where the reduced form is colourless or less intense colour and the oxidized form shows intense colour. A redox indicator in solution establishes a redox equilibrium by its own character with a specific electrode potential as:



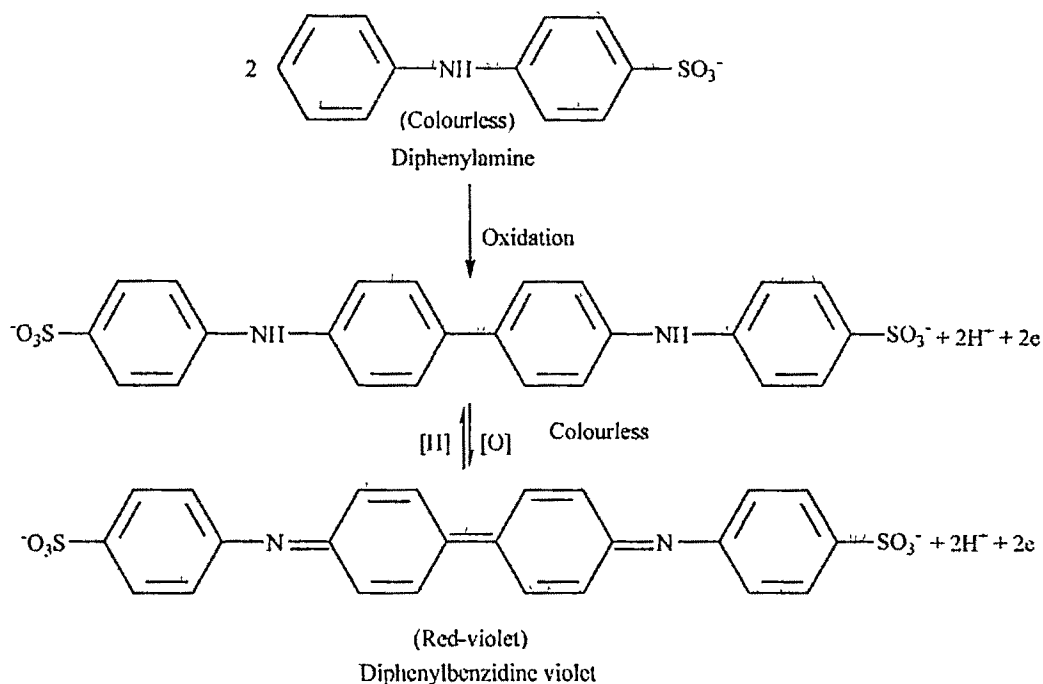
$$E = E_{\text{In}}^f + \frac{0.0591}{n} \log \frac{[\text{In}_{\text{ox}}]}{[\text{In}_{\text{red}}]} \text{ at } 25^\circ \text{C}$$

To exhibit the colour of the oxidized form, $[\text{In}_{\text{ox}}] / [\text{In}_{\text{red}}]$ should be ≥ 10 and to exhibit the colour of the reduced form $[\text{In}_{\text{red}}] / [\text{In}_{\text{ox}}]$ should be ≥ 10 . Hence the colour change can be detected at the potential range, called transition potential (E_{tp}) of an indicator and is given by

$$E_{\text{tp}} = E_{\text{In}}^f \pm 0.0591/n$$

Therefore, a rightly chosen indicator's transition potential should lie within the equivalence potential range of the titrating systems. As for example, diphenylamine sulphonate undergoes a reversible change of structure due to oxidation when higher potential avails from the titration process and therefore, shows colour change.

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In order to get best result of identification of equivalence point from the indicator, E_{tp} of the indicator should lie close to that of the potential at the equivalence point (E_{eq}) of the redox systems under titration. Thus, $E_{\text{tp}} \cong E_{\text{eq}}$

$$\text{i.e. } mE_1^f + nE_2^f / m+n = E_{\text{In}}^f \pm 0.0591/n$$

Some useful redox indicators and related properties :

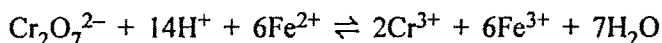
Indicators	Colour		E_{In}^f V [in ($\text{H}^+ = 1(\text{M})$)}
	In _{ox}	In _{red}	
Methylene blue	Blue	Colourless	0.53
Diphenylamine	Blue-violet	Colourless	0.76
Diphenylbenzidine	Blue-violet	Colourless	0.76
Diphenylamine sulphonic acid	Red-violet	Colourless	0.85
N-phenylanthranilic acid	Red-violet	Colourless	1.08
Ferriin (Fe^{2+} -phenanthroline complex)	Pale-blue	Red	1.06

Essentially the indicator should be oxidized as close to the equivalence point as possible, neither too early, nor too late. So the potential range of the indicator, for detection of equivalence point through sudden sharp colour change, should lie within the limits of the sharp change of potentials at the equivalence point as shown in the titration curve (segment b, Fig. 1.3(i)). Therefore, for fair selection of a redox indicator for a particular redox titration, the following conditions must have to be fulfilled.

$$(i) E_{Ox}^f > E_{In}^f > E_{Red}^f \quad (ii) E_{eq} \cong E_{tp}$$

The selection of right indicator in a particular titration may be illustrated as :

Let, Fe^{2+} will be estimated by titrating with standard $K_2Cr_2O_7$ solution in 1(N) H_2SO_4 . The overall reaction is :



$$\text{And } E_{eq} = \left(\frac{6E_{(Cr_2O_7^{2-}/2Cr^{3+})}^f + E_{(Fe^{3+}/Fe^{2+})}^f}{(6+1)} \right) = (6 \times 1.33 + 1 \times 0.77) / 7 = 1.25 \text{ V.}$$

In fact, the potential shifts at the equivalence point lies in the range 0.95V to 1.30V. Hence, the indicator that to be chosen must have the E_{tp} (i.e. the potential range of the indicator) in this range. So, diphenylamine ($E_{In}^f = 0.76V$) or diphenylaminesulphonic acid ($E_{In}^f = 0.85V$) can not be used as their E^f values show that the colour change will occur before the arrival of the equivalence point. But, if H_3PO_4 or NH_4HF_2 is added before titration, due to complex formation with the Fe^{3+} ion, the formal potential of the Fe^{3+}/Fe^{2+} will get lowered than transition potential (E_{tp}) of the indicator like diphenylamine or its sulphonate derivative. Also, in this situation final lowered equivalence potential (E_{eq}) lies in the close vicinity of the transition potential (E_{tp}) of the indicator. It may also be inferred that N-phenylanthranilic acid may be used in the above titration without addition of any complexing agents.

It is necessary to mention here about the dual property of functioning of $KMnO_4$ solution both as a good oxidant and as a self indicator. The titration of Fe^{2+} ($E_{Fe^{3+}/Fe^{2+}}^0 = 0.77V$) by $KMnO_4$ ($E_{MnO_4^-/Mn^{2+}}^0 = 1.51V$) in 1–2 (N) H_2SO_4 medium using H_3PO_4 to mask the yellow colour of produced Fe^{3+} in medium, requires no use of any indicator. Because one drop of excess MnO_4^- solution (concentration of $MnO_4^- = 0.05N$) just after the equivalence point is sufficient to develop an observable faint pink colour of the titrated solution which indicates that the equivalence point (end point) is over. So, in permanganometric titration usually no further indicator is used for the above reason.

Permanganometric Titration

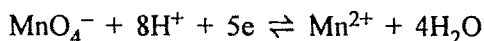
2.1 General Discussion :

Potassium permanganate is a very powerful and widely used oxidising agent to oxidize many reducing agents in different conditions to estimate the amount of reducing materials. The redox

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titration with potassium permanganate solution as an oxidant is called permanganometric titration or permanganometry. The power of KMnO_4 as an oxidant depends on the pH of the medium.

(i) In acid medium it shows a very high degree of oxidizing power.



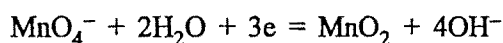
$$E = E^0 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]} \text{ at } 25^\circ\text{C}$$

$$E = E^0 + \frac{0.0591}{5} \log [\text{H}^+]^8 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

So, the reduction potential of the $\text{MnO}_4^-/\text{Mn}^{2+}$ system depends on H^+ concentration and concentration ratio of MnO_4^- and Mn^{2+} ions in solution. At standard state i.e., $[\text{H}^+] = 1\text{ mol/lit}$, $[\text{MnO}_4^-] = [\text{Mn}^{2+}] = 1\text{ mole/lit}$ and 25°C , the potential of the system, $E = E^0 =$ standard reduction potential = 1.51V (observed value). The equivalent weight of KMnO_4 in this situation = formula weight/5 = $158.03/5 = 31.606$.

H_2SO_4 is the most suitable acid to serve H^+ in dilute solution. HCl reacts with MnO_4^- as: $2\text{MnO}_4^- + 10\text{Cl}^- + 16\text{H}^+ = 2\text{Mn}^{2+} + 5\text{Cl}_2 + 6\text{H}_2\text{O}$. HNO_3 , itself an oxidant, reacts with reducing agents used in the permanganometry.

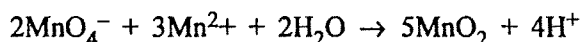
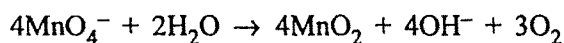
(ii) In neutral or faintly alkaline medium the oxidizing power of KMnO_4 reduces, as the standard reduction potential E^0 of the reaction system is 0.59V (p 24) which is lower than the above. The equivalent weight of KMnO_4 is = $158.03/3 = 52.677$.



(iii) In alkaline medium the oxidizing power is still less as is seen by the potential $E^0 = 0.56\text{V}$ of the reaction process. The equivalent weight of KMnO_4 in this situation is equal to its molecular weight, i.e., 158.03.



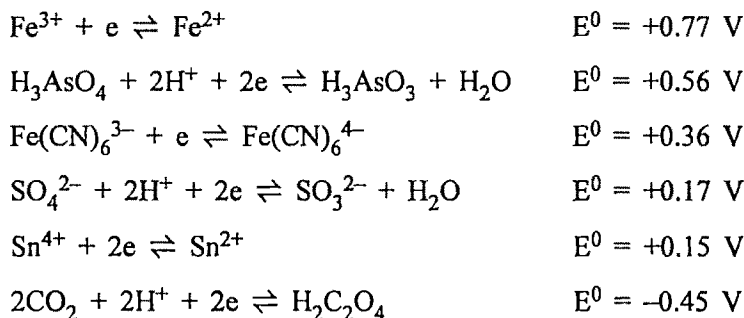
By nature KMnO_4 is very reactive and is not a primary standard substance due to always contamination of trace MnO_2 . Mn^{2+} , MnO_2 , light or a trace organic matter catalyses the decomposition of KMnO_4 in solution:



The rate of decomposition is slow in acid medium but rapid in neutral medium. For this reason KMnO_4 solution can not be stored ordinarily for a long period of time. It also reacts with the reducing matters present in filter papers or rubber cocks etc. If required,

KMnO₄ solution should be filtered through a funnel containing purified glass wool or through a sintered glass crucible. For precaution KMnO₄ solution is prepared by specially purified distilled water.

Being a stronger oxidant it may be used to titrate many reductants having potential lower at least by 0.2V with respect to MnO₄⁻/Mn²⁺ system (1.51V). A few examples of such reactions are given by the equations:



Due to strong charge transfer absorption, MnO₄⁻ itself has a very intense violet/pink colour in solution. Even the presence of one drop of KMnO₄ solution of strength 0.05(N) in one litre of distilled water exhibits a distinguishable faint pink colour of the solution. As a result, permanganometry needs no redox indicator, provided the titrating medium is colourless. After the equivalence point, addition of one drop of excess KMnO₄ solution imparts faint pink colour of the solution indicating the end point of the titration. Thus, KMnO₄ acts as a self indicator.

2.2. Specifications :

A. Preparation of 0.05(N) KMnO₄ solution: To prepare 0.05(N) one litre solution, about 1.6 g pure grade KMnO₄ is weighted out on a watch glass by an ordinary balance and transfer the entire solid into a 500 ml clean beaker using a small portion of one litre distilled water taking in a measuring cylinder. Stir with a glass rod to allow to dissolve. KMnO₄ crystals dissolve slowly. The violet colour solution is filtered through a funnel containing purified glass wool or through a sintered glass crucible by slow decantation process. The dissolution by stirring and then filtration through decantation by taking a small portion of the same measured volume of water is done repeatedly in same manner such that all crystals of KMnO₄ dissolve in that one litre of water. Finally the homogeneous solution is stored in a clean glass-stoppered dark brown coloured glass bottle. The solution is a secondary standard and needs standardization each time before or after use.

B. Standardization of KMnO₄ solution :

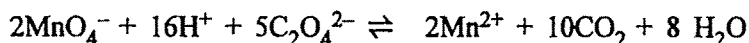
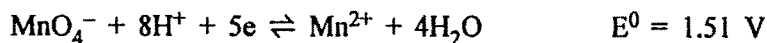
KMnO₄ solution may be standardized by titration with any one of the following primary standard solutions : (i) oxalic acid or sodium oxalate (ii) Mohr's salt (iii) Arsenious oxide (iv) Potassium ferrocyanide.

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Standardization of KMnO_4 with standard oxalic acid solution :

Theory :

In hot 2(N) H_2SO_4 medium KMnO_4 oxidizes $\text{C}_2\text{O}_4^{2-}$ (oxalate ion) to CO_2 quantitatively.



The equivalence point is identified by the faint pink colour of one drop excess solution acting as autoindicator.

\therefore Equivalent weight of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) = $126/2 = 63.0$

To prepare 250ml (N/20) oxalic acid solution, weight of oxalic acid to be taken is $63.0 \times 250/1000 \times 20 = 0.7875\text{g}$.

Equivalent weight of $\text{Na}_2\text{C}_2\text{O}_4 = 134/2 = 67$. So, 0.8375 g $\text{Na}_2\text{C}_2\text{O}_4$ is to be taken in 250 ml water for (N/20) solution.

Chemicals required : (i) Standard (N/20) oxalic acid or standard (N/20) sodium oxalate solution.

(ii) (N/20) KMnO_4 solution: 0.4 – 0.5 g of KMnO_4 per 250 ml of solution.

(iii) 2(N) H_2SO_4 solution.

Procedure : 25 ml aliquot of standard oxalic acid solution is pipetted out into a 500 ml conical flask. 150 ml 2(N) H_2SO_4 is added, the mixture is heated on a wire gauge/asbestos board to about 70-80°C and is titrated with KMnO_4 solution running from the burette drop wise. Disappearance of pink colour is slow at the beginning, then becomes rapid as Mn^{2+} produced catalyses the reaction (autocatalyst). The end point is identified by just appearance of faint pink colour lasting for at least 30 seconds for a drop of excess KMnO_4 solution. As the KMnO_4 solution is deep coloured the upper meniscus of burette reading is noted. To get the concordant reading the experiment is repeated.

Experimental Data :

No. of titrations	Vol. of standard oxalic acid taken (ml)	Burette reading of KMnO_4 solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

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Calculation : According to the principles of reaction,

$$V_1 \times S_1 = V_2 \times S_2 \quad \text{or, } S_1 = V_2 S_2 / V_1$$

where, V_1 = volume of resultant KMnO_4 in titration, S_1 = strength of KMnO_4 , V_2 = volume of oxalic acid taken in titration, S_2 = strength of oxalic acid.

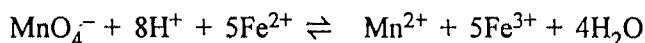
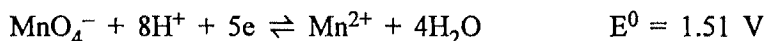
$$\text{or, } 1000 \text{ ml (N) oxalic acid} = 31.6 \text{ g KMnO}_4$$

C. The use of standard KMnO_4 in volumetric estimation :

(I) Estimation of Ferrous iron in Mohr's salt :

Theory :

In dilute sulphuric acid medium KMnO_4 acts as a powerful oxidant and oxidizes Fe^{2+} to Fe^{3+} rapidly and quantitatively.



Here KMnO_4 acts as a self indicator. But yellow colour of Fe^{3+} interferes to observe the faint pink colour of Mn^{2+} at the equivalence point. To overcome the problem H_3PO_4 or NH_4HF_2 is used to mask the yellow colour of Fe^{3+} by forming colourless $[\text{Fe}(\text{HPO}_4)]^+$ or $[\text{FeF}_6]^{3-}$ complex in solution. From the reaction $\text{MnO}_4^- / 5 = \text{Fe}^{2+} / 1$

$$\therefore 1000 \text{ ml (N) KMnO}_4 \equiv 55.85 \text{ g Fe}^{2+}.$$

Chemicals required :

- (i) Standard (N/20) oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ or standard sodium oxalate (N/20) solution.
- (ii) (N/20) KMnO_4 solution: 0.4 – 0.5 g of KMnO_4 per 250 ml.
- (iii) 2(N) H_2SO_4
- (iv) Syrupy H_3PO_4 acid or solid NH_4HF_2
- (v) (N/20) Mohr's salt solution : ~ 5 g of Mohr's salt per 250 ml in 2(N) H_2SO_4 .

Procedure : 25 ml aliquot of Mohr's salt solution is pipetted out into a 500 ml conical flask. 125 ml 2(N) H_2SO_4 , 5 ml H_3PO_4 / ~2g NH_4HF_2 are added and the resulting mixture is titrated with KMnO_4 solution running from the burette until a faint pink colour persisting at least 30 seconds is obtained, that indicates the end point of the titration. The experiment is repeated to get concordant readings. H_3PO_4 helps to get sharp end point and H_2SO_4 to maintain H^+ ions and potentials.

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Experimental Data :

(a) Standardization of supplied $\sim(N/20)$ KMnO_4 solution :

No. of titrations	Vol. of standard oxalic acid taken (ml)	Burette reading of KMnO_4 solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

(b) Estimation of Fe^{2+} iron in Mohr's salt by standard KMnO_4 solution :

No. of titrations	Vol. of standard oxalic acid taken (ml)	Burette reading of KMnO_4 solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

Calculation :

Let, (i) an accurate weight of oxalic acid taken to prepare 250 ml $(N/20)$ oxalic acid solution = W g

$$\therefore \text{Strength of oxalic acid} = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{0.7875 \left(\frac{N}{20} \right)} = \frac{W}{0.7875 \times 20} (N) = S(N)$$

(ii) For 25 ml $S(N)$ oxalic acid, volume of KMnO_4 required in titration = V_{st} ml

$$\begin{aligned} \therefore \text{Strength of } \text{KMnO}_4 &= \frac{25 \times S(N)}{V_{st}} = \frac{25}{V_{st}} \times \frac{W}{0.7875 \times 20} (N) \\ &= 1.5873 \times \frac{W}{V_{st}} (N) = f(N) \end{aligned}$$

(iii) For 25 ml supplied Mohr's salt, volume of KMnO_4 in titration required = V_{Fe} ml

$$1000 \text{ ml of } (N) \text{ } \text{KMnO}_4 \equiv 55.85 \text{ g } \text{Fe}^{2+}$$

$$V_{Fe} \text{ ml } f(N) \text{ } \text{KMnO}_4 \text{ solution} = (0.05585 \times V_{Fe} \times f) \text{ g } \text{Fe}^{2+}$$

$$25 \text{ ml Mohr's salt solution contains} = (0.05585 \times V_{Fe} \times f) \text{ g } \text{Fe}^{2+}$$

$$\therefore 1000 \text{ ml Mohr's salt solution contains} = (0.05585 \times V_{Fe} \times f \times 40) \text{ g } \text{Fe}^{2+}$$

$$= 0.05585 \times 40 \times V_{Fe} \times 1.5873 \times \frac{W}{V_{st}} \text{ g } \text{Fe}^{2+}$$

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∴ Therefore, Fe^{2+} iron present in supplied Mohr's salt solution $= 3.54603 \times W \times \frac{V_{\text{Fe}}}{V_{\text{st}}}$ g / L In case of Mohr's salt,

1000 ml (N) KMnO_4 solution \equiv 392 g Mohr's salt

V_{Fe} ml f (N) KMnO_4 solution $\equiv (0.392 \times V_{\text{Fe}} \times f)$ g Mohr's salt

Mohr's salt present in supplied 25 ml solution $= (0.392 \times V_{\text{Fe}} \times f)$ g

∴ Mohr's salt present in supplied 1000 ml solution $= 0.392 \times 40 \times V_{\text{Fe}} \times 1.5873 \times \frac{W}{V_{\text{st}}}$ g/L

∴ Therefore, Mohr's salt present in supplied solution is $= 24.8888 \times W \times \frac{V_{\text{Fe}}}{V_{\text{st}}}$ g/L

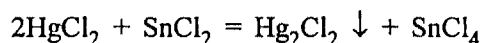
(ii) Estimation of Ferric iron in Ferric salt :

Theory :

Ferric iron (Fe^{3+}) is first reduced to ferrous iron (Fe^{2+}) in hot HCl medium quantitatively either by the use of (i) SnCl_2 solution or by (ii) Al foil. The reactions are :

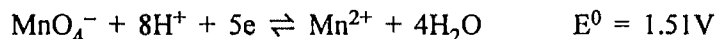


In case (i), the excess SnCl_2 is destroyed by adding excess HgCl_2 solution

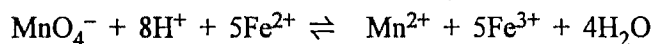


In case (ii), the excess disintegrated Al is dispelled by boiling.

The Cl^- present in the system will react with KMnO_4 , so to stop the side reaction and to protect KMnO_4 Zimmermann Reinhardt (ZR) solution consisting of MnSO_4 , H_3PO_4 and H_2SO_4 , called preventive solution is used prior to start of the titration.



Then, the acidity of the solution is adjusted to about 2(N) and finally the Fe^{2+} is titrated with rapid addition of standard KMnO_4 solution, the end point is indicated by the appearance of first faint pink colour for one drop of excess KMnO_4 solution.



$$\therefore \frac{\text{MnO}_4^-}{5} = \frac{\text{Fe}^{2+}}{1} = \frac{\text{Fe}^{3+}}{1}$$

1000 ml of (N) $\text{KMnO}_4 \equiv 55.85$ g Fe^{3+}

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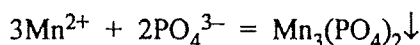
The functions of Zimmermann Reinhardt (ZR) solution :

1. MnSO_4 : It serves excess Mn^{2+} ions, as a result the formal potential of $\text{MnO}_4^- / \text{Mn}^{2+}$ system falls below 1.36 V of $\text{Cl}_2 / 2\text{Cl}^-$ system. Therefore, MnO_4^- can no longer oxidize Cl^- to Cl_2 , i.e.

$$E = E^0 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]} < 1.36 \text{ V.}$$

2. H_3PO_4 : It removes yellow colour of Fe^{3+} by forming colourless soluble $[\text{Fe}(\text{HPO}_4)]^+$ complex, as a result (i) the reduction potential of $\text{Fe}^{3+} / \text{Fe}^{2+}$ falls below 0.77V which is favourable for MnO_4^- to oxidize Fe^{2+} easily. (ii) the detection of sharp end point becomes possible for removal of colour interference.

3. H_2SO_4 : It maintains the required acidity and hence potentials. Further it prevents the precipitation of manganese phosphate of ZR solution by increasing its solubility.



Chemicals required :

- (i) (N/20) KMnO_4 solution : 0.4 – 0.5 g of KMnO_4 per 250 ml solution.
- (ii) For ~ (N/20) Fe^{3+} solution: In case of (a) ferric alum, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (F.W. = 964.3). 24 g is dissolved in 0.1(N) H_2SO_4 to get 1000 ml solution; (b) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (F.W. = 270). 13.5 g in 100 ml conc. HCl and dilute to 1000 ml with water.
- (iii) ZR solution: 50 g $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ is dissolved first in 250 ml water. Then 100 ml conc. H_2SO_4 , 300 ml water and 100 ml syrupy H_3PO_4 are added carefully to get 750 ml ZR solution.
- (iv) SnCl_2 solution: 30 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is dissolved in 100 ml conc. HCl by heating and then by adding water, 200 ml solution is prepared. A few pieces of metallic tin is kept into the solution for prevention of oxidation of Sn^{2+} to Sn^{4+} .
- (v) HgCl_2 solution : 5% standard solution is prepared by dissolving 5 g salt in 100 ml water
- (vi) Al-foil.

Procedure :

(a) Reduction of Fe^{3+} by SnCl_2 and then titration :

25 ml of Fe^{3+} solution is pipetted out into a 500 ml conical flask, 25 ml conc. HCl is added and the flask is heated on an wire gauge/asbestos board to 80-90°C. Drop by drop SnCl_2 solution is added to yellow Fe^{3+} solution with constant shaking until yellow colour of the solution just disappears. One drop diluted SnCl_2 (1:2) solution is added in excess. The flask with the solution is rapidly cooled under tap water to attain room temperature. 10ml 5% HgCl_2 solution is added at a time with shaking the flask and then allowed to stand one minute when a slight silky

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white precipitate of Hg_2Cl_2 appears. The solution is diluted to 200 ml with distilled water, 20 ml ZR solution is added and the final mixture is titrated with standard KMnO_4 solution running from the burette until a faint pink colour of the solution lasting at least for 20 seconds is obtained. The titration is repeated for concordant results.

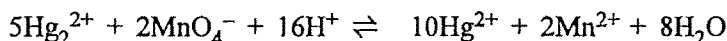
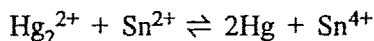
(b) Reduction of Fe^{3+} by Al and then titration :

25 ml of Fe^{3+} solution is pipetted out into a 500 ml conical flask, 30 ml conc. HCl is added and the flask is heated to $80^\circ\text{--}90^\circ\text{C}$ on a wire gauge/asbestos board. Then small Al-foils are introduced step by step swirling the solution until the yellow colour of Fe^{3+} solution just disappears with the formation of a colourless and clear solution through boiling. 100 ml distilled water is added immediately and cooled to room temperature rapidly under the tap water. 20 ml ZR solution is added and the final mixture is titrated with standard KMnO_4 solution running from the burette until a faint pink colour of the solution lasting at least for 20 seconds is obtained. The titration is repeated for concordant results.

Experimental Data and Calculation: As earlier.

Precautions :

- (i) SnCl_2 used for reduction of Fe^{3+} should not add much in excess, because it reacts with HgCl_2 and produce a heavy white precipitate of Hg_2Cl_2 or a grey precipitate of Hg which may consume used KMnO_4 in titration.



- (ii) FeCl_3 is a volatile substance, so boiling of the solution with HCl should not be done.
- (iii) The faint pink colour of KMnO_4 after the end point fades rapidly after a few seconds due to many side reactions of KMnO_4 with other reductants like Hg_2^{2+} , Cl^- , Mn^{2+} etc. of the system. So the titration should be done rapidly. Slow titration invites errors.

(iii) Estimation of Ferrous and Ferric Iron in a mixture :

For Fe^{2+} : As Fe^{3+} does not react with KMnO_4 , Fe^{2+} in presence of Fe^{3+} may easily be titrated with standard KMnO_4 solution directly by taking 25 ml aliquot of the supplied solution and following the procedure as Mohr's salt titration earlier. The volume of KMnO_4 obtained from the titration corresponds to the amount of Fe^{2+} iron present into that aliquot.

For Fe^{3+} : As Fe^{3+} does not react with KMnO_4 , it may be estimated indirectly as follows: 25 ml of the aliquot of the mixture of Fe^{3+} and Fe^{2+} is reduced first with Al-foil/ SnCl_2 solution in hot HCl medium and the total Fe^{2+} iron of the mixture will be titrated with standard KMnO_4 solution as discussed earlier. The volume of KMnO_4 titre value corresponds to total (Fe^{3+} and Fe^{2+}) iron, present into that 25 ml aliquot. Subtracting the amount of Fe^{2+} from the total amount of ($\text{Fe}^{3+} + \text{Fe}^{2+}$) iron, the amount of Fe^{3+} can be obtained. The procedure, experimental data, calculations etc are similar as earlier.

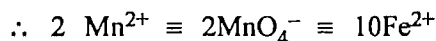
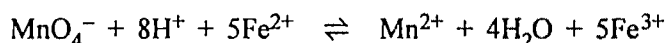
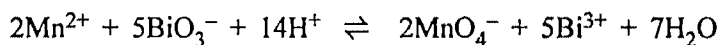
(iv) Estimation of manganese in manganese sulphate solution:

Mn^{2+} in MnSO_4 solution is estimated either (i) by oxidizing it to MnO_4^- with the use of NaBiO_3 in H_2SO_4 medium or (ii) by oxidizing it to solid MnO_2 using KBrO_3 in H_2SO_4 medium. Both methods are useful and quantitative. The later method is less hazardous.

(1) Oxidation of Mn^{2+} by NaBiO_3 :

Theory :

In 2(N) H_2SO_4 medium NaBiO_3 oxidizes Mn^{2+} to MnO_4^- quantitatively in cold. The MnO_4^- produced is estimated by adding measured excess standard Mohr's salt solution and back titrating the excess Mohr with a standard KMnO_4 solution.



$$\frac{\text{Mn}^{2+}}{5} = \frac{\text{MnO}_4^-}{5} = \text{Fe}^{2+}$$

$$\therefore 1000 \text{ ml of (N) Mohr's salt solution} \equiv 10.988 \text{ g Mn}^{2+}$$

Chemicals required :

- (i) For a (N/20) Mn^{2+} solution: (a) $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (F.W. = 169): 1.7 g salt + 20 ml distilled water + 10 ml C. H_2SO_4 and the solution is diluted to 1000 ml. (b) $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (F.W. = 223): 2.2 g salt + 20 ml distilled water + 15 ml C. H_2SO_4 and the mixture is diluted to 1000 ml.
- (ii) Solid NaBiO_3
- (iii) Mohr's salt solution (N/20)
- (iv) 2(N) H_2SO_4
- (v) Syrupy H_3PO_4
- (vi) Standard (N/20) oxalic acid solution
- (vii) (N/20) KMnO_4 solution

Procedure : 25 ml Mn^{2+} solution is pipetted out into a 250 ml beaker and diluted it to 100 ml by distilled water. 5ml conc. H_2SO_4 is added and stirred with a glass rod. The beaker with the solution is placed in ice bath to cool to about 10°C . Approximately 1.0 g NaBiO_3 is added in fractions with constant stirring for 2-3 minutes to oxidize Mn^{2+} to MnO_4^- (pink colour solution) completely. The excess solid NaBiO_3 remain undissolved and settled at the bottom. A measured excess of 50 ml standard Mohr's salt solution is taken in a 500ml Buchner flask, a G-4 marked sintered glass crucible is fitted tightly with an adapter at the mouth of the Buchner flask and

finally it is connected to the water suction. The pink MnO_4^- solution is then filtered through the glass crucible. The beaker and the crucible are washed with cold 2(N) H_2SO_4 using 5-10 ml each time until the filtrate is colourless. 5 ml syrupy H_3PO_4 is added and the excess Mohr's salt is back titrated with the standard KMnO_4 solution.

Experimental Data :

(a) Standardization of KMnO_4 solution : As usual

(b) Standardization of Mohr's salt solution : As usual

(c) Estimation of Mn^{2+} by back titration with standard KMnO_4 solution :

No. of titrations	Vol. of supplied Mn^{2+} (ml)	Volume of Mohr's salt solution (ml)	Burette reading of standard KMnO_4 solution (ml)			
			Initial	Final	Difference	Most frequent reading
1	25	50				
2	25	50				
3	25	50				

Calculation :

Let,

(i) an accurate weight of oxalic acid taken for 250 ml (N/20) solution = W g.

$$\therefore \text{Strength of oxalic acid} = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{0.7875} (\text{N} / 20) = S(\text{N})$$

(ii) 25 ml S(N) oxalic acid = V_{st} ml KMnO_4 solution

$$\therefore \text{Strength of } \text{KMnO}_4 = \frac{25 \times S}{V_{\text{st}}} (\text{N}) = \frac{25}{V_{\text{st}}} \times \frac{W}{0.7875 \times 20} (\text{N}) = 1.5873 \times \frac{W}{V_{\text{st}}} (\text{N}) = f(\text{N})$$

(iii) 25 ml Mohr's salt solution = V_1 ml $f(\text{N})$ KMnO_4 solution

$$\therefore 50 \text{ ml Mohr's salt solution} = 2V_1 \text{ ml } f(\text{N}) \text{ } \text{KMnO}_4 \text{ solution}$$

(iv) For back titration of excess Mohr's salt solution, the volume of standard KMnO_4 of strength $f(\text{N})$ required = V_2 ml.

Therefore, we may write,

Vol. of MnO_4^- coming from the reaction mixture + V_2 ml $f(\text{N})$ $\text{KMnO}_4 \equiv 50$ ml Mohr's salt solution $\equiv 2V_1$ ml $f(\text{N})$ KMnO_4

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∴ Volume of MnO_4^- coming from the reaction mixture $\equiv (2V_1 - V_2)$ ml f(N) KMnO_4 .

1000 ml of (N) $\text{KMnO}_4 \equiv 10.988 \text{ g Mn}^{2+}$

∴ $(2V_1 - V_2)$ ml f(N) $\text{KMnO}_4 = 0.010988 \times (2V_1 - V_2) \times f \text{ g Mn}^{2+}$

25 ml supplied solution contains $= 0.010988 \times (2V_1 - V_2) \times f \text{ g Mn}^{2+}$

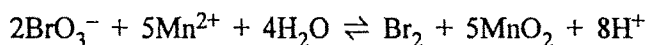
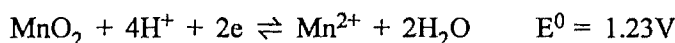
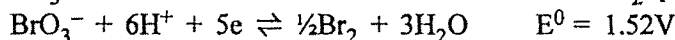
∴ 1000 ml supplied solution contains $= 0.010988 \times (2V_1 - V_2) \times f \times 40 \text{ g Mn}^{2+}$

$$\begin{aligned} \text{Therefore, Mn}^{2+} \text{ present in supplied solution} &= 0.010988 \times 40 \times (2V_1 - V_2) \times 1.5873 \times \frac{W}{V_{st}} \text{ g/L} \\ &= 0.69765 \times W \times \frac{2V_1 - V_2}{V_{st}} \text{ g/L} \end{aligned}$$

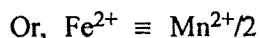
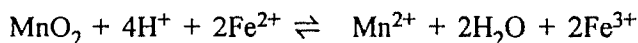
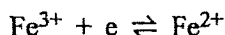
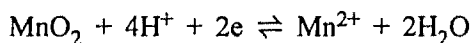
(2) Oxidation of Mn^{2+} by KBrO_3 :

Theory :

In 4(N) H_2SO_4 medium KBrO_3 oxidizes Mn^{2+} to insoluble black solid of MnO_2 quantitatively in boiling condition.



The produced MnO_2 is estimated by adding measured excess standard Mohr's salt solution and back titrating the excess Mohr with a standard KMnO_4 solution.



1000 ml (N) Mohr's salt solution $\equiv 1000\text{ml (N) KMnO}_4 \equiv 54.94/2 \text{ g Mn}^{2+} \equiv 27.47\text{g Mn}^{2+}$

Chemical required :

(i) For a (N/20) Mn^{2+} solution : (a) $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (F.W.=169) : 4.2 g salt + 20 ml distilled water + 15 ml C. H_2SO_4 and the solution is diluted to 1000 ml. (b) $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (F.W.=223) : 5.5 g salt + 20 ml distilled water + 15 ml C. H_2SO_4 and the mixture is diluted to 1000 ml. (ii) 5% KBrO_3 solution: Dissolve 5g KBrO_3 in 100 ml boiling water with stirring. (iii) (N/20) Mohr's salt solution, (iv) 4(N) H_2SO_4 , (v) Syrupy H_3PO_4 , (vi) Standard (N/20) oxalic acid solution, (vii) (N/20) KMnO_4 solution.

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Procedure : 25 ml of the supplied Mn^{2+} solution is pipetted out into a 250 ml beaker, added 10 ml 4(N) H_2SO_4 followed by 10 ml 5% KBrO_3 solution. The mixture is boiled gently for 20 minutes taking a glass rod and keeping the beaker covered with a watch glass and water added to replenish the loss by boiling. Allow the mixture to cool to room temperature and filter carefully through Whatman 42 filter paper. The beaker and the filter paper containing the precipitate is washed thoroughly with boiling distilled water using 5 ml portions each time with the help of a dropper till the precipitate free from BrO_3^- (tested washing liquid with very dilute $\text{HCl} + \text{KI} + \text{starch}$ solution). The precipitate with the filter paper is transferred into the original beaker, 25 ml 4(N) H_2SO_4 is added followed by exact 50 ml of standardized Mohr's salt solution by means of a pipette. Stirred till the black MnO_2 dissolves (neglect if a trace blackish portion is seen). 2 g NH_4HF_2 or 5 ml syrupy H_3PO_4 is added and the mixture is titrated with standard KMnO_4 solution as usual.

Experimental Data :

Calculation :

Let, (i) an accurate weight of oxalic acid taken for 250 ml (N/20) solution = W g.

$$\therefore \text{Strength of oxalic acid} = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{0.7875} (\text{N} / 20) = \text{S(N)}$$

(ii) 25 ml S(N) oxalic acid = V_{st} ml KMnO_4 solution

$$\therefore \text{Strength of } \text{KMnO}_4 = \frac{25 \times \text{S}}{V_{\text{st}}} (\text{N}) = \frac{25}{V_{\text{st}}} \times \frac{W}{0.7875 \times 20} (\text{N}) = 1.5873 \times \frac{W}{V_{\text{st}}} (\text{N}) = \text{f(N)}$$

(iii) 25 ml Mohr's salt solution = V_1 ml f(N) KMnO_4 solution

\therefore 50 ml Mohr's salt solution = $2V_1$ ml f(N) KMnO_4 solution

(iv) For back titration of excess Mohr's salt solution, the volume of standard KMnO_4 of strength f(N) required = V_2 ml.

Therefore, we may write, the amount of MnO_2 coming from the reaction + V_2 ml f(N) $\text{KMnO}_4 \equiv$ 50 ml Mohr's salt solution $\equiv 2V_1$ ml f(N) KMnO_4

\therefore The amount of MnO_2 coming from the reaction $\equiv (2V_1 - V_2)$ ml f(N) KMnO_4 .

1000ml of (N) $\text{KMnO}_4 \equiv 27.47 \text{ g } \text{Mn}^{2+}$

$\therefore (2V_1 - V_2)$ ml f(N) $\text{KMnO}_4 = 0.02747 \times (2V_1 - V_2) \times \text{f g } \text{Mn}^{2+}$

25 ml supplied solution contains = $0.02747 \times (2V_1 - V_2) \times \text{f g } \text{Mn}^{2+}$

\therefore 1000 ml supplied solution contains = $0.02747 \times 40 \times (2V_1 - V_2) \times \text{f g } \text{Mn}^{2+}$

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$$\begin{aligned}\text{Therefore, Mn}^{2+} \text{ present in supplied solution} &= 0.02747 \times 40 \times (2V_1 - V_2) \times 1.5873 \times \frac{W}{V_{st}} \text{ g/L} \\ &= 1.744125 \times W \times \frac{2V_1 - V_2}{V_{st}} \text{ g/L}\end{aligned}$$

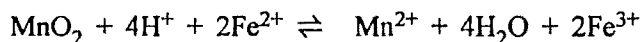
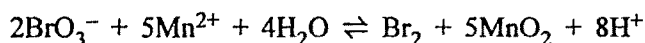
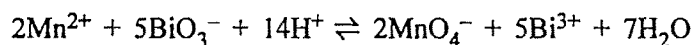
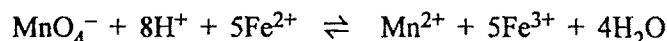
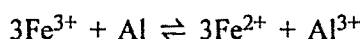
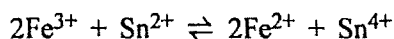
(v) Estimation of Manganese of other sources :

Accurately weighed solid Mn-sample is digested first in 1:1 HCl by boiling and the almost dried mass is then heated with Conc. H_2SO_4 gently to expel HCl completely. After cooling the digested product containing H_2SO_4 is diluted and boiled to dissolve the MnSO_4 salt. Taking the solution quantitatively manganese may be estimated by following any oxidation method as discussed earlier.

(vi) Estimation of Fe^{3+} and Mn^{2+} in a mixture :

Theory :

As Mn^{2+} does not interfere Fe^{3+} can be directly estimated in presence of Mn^{2+} by titration with standard KMnO_4 solution in presence of ZR solution after reduction of Fe^{3+} either by the use of SnCl_2 and HgCl_2 or by Al-foil as discussed earlier. Mn^{2+} can also be estimated in presence of Fe^{3+} after oxidation of Mn^{2+} in acid medium either (i) by NaBiO_3 to MnO_4^- or by (ii) KBrO_3 to MnO_2 as discussed earlier. So separation of iron from manganese is not required. The reactions are:



$$1000 \text{ ml of (N) } \text{KMnO}_4 \equiv 55.85 \text{ g } \text{Fe}^{3+}$$

$$\equiv 10.988 \text{ g } \text{Mn}^{2+} \text{ (in case of } \text{MnO}_4^-; \text{NaBiO}_3 \text{ oxidation)}$$

$$\equiv 27.47 \text{ g } \text{Mn}^{2+} \text{ (in case of } \text{MnO}_2; \text{KBrO}_3 \text{ oxidation)}$$

Chemical required :

(i) Fe^{3+} solution ($\sim \text{N}/10$)

(ii) Mn^{2+} solution ($\sim \text{N}/10$) and mix (i) and (ii) in equal volume to get Fe^{3+} and Mn^{2+} ($\text{N}/20$)

(iii) Standard ($\text{N}/20$) oxalic acid solution

(iv) ($\text{N}/20$) KMnO_4 solution

(v) Z-R solution

(vi) Al-foil

(vii) 4(N) H_2SO_4 , (viii) 5% KBrO_3 solution/ NaBiO_3 (s), (ix) (N/20) Mohr's salt solution

Procedure :

Estimation of Fe^{3+} : 25 ml of the supplied solution containing Fe^{3+} is pipetted into a 500 ml conical flask and 30 ml conc. HCl is added. The solution is heated near to boiling and introduced a few small pieces of Al-foils swirling the solution until the reduction of yellow Fe^{3+} is complete with the formation of a colourless and clear solution by boiling. 100 ml water is added and cool the flask to room temperature rapidly under tap water. 20 ml ZR solution is added and the mixture is titrated with standard KMnO_4 solution as usual. Repeat the titration to get a concordant result.

Estimation of Mn^{2+} : 25 ml of the supplied solution containing Mn^{2+} is pipetted out into a 250 ml beaker. 10 ml 4(N) H_2SO_4 is added followed by 10 ml 5% KBrO_3 solution. The mixture is boiled gently for 20 minutes taking a glass rod and keeping the beaker covered with a watch glass, water is added to replenish that loss by boiling. Allow the mixture to cool to room temperature and filter carefully through Whatman 42 filter paper. Wash the beaker and the precipitate thoroughly with boiling distilled water using 5 ml portions each time with the help of a dropper till the precipitate free from BrO_3^- (tested washing liquid with dilute $\text{HCl} + \text{KI} + \text{starch}$ solution). The precipitate with the filter paper is transferred into the original beaker, added 25 ml 4(N) H_2SO_4 followed by exact 50 ml of standardized Mohr's salt solution by means of a pipette. Stirred till the black MnO_2 dissolves (neglect if a trace blackish portion is seen). 5 ml $\text{H}_3\text{PO}_4/2 \text{ g NH}_4\text{HF}_2$ is added and titrated the mixture with standard KMnO_4 solution as usual.

Experimental Data : As usual

Calculation :

Let, (i) an accurate wt. of oxalic acid taken for 250 ml (N/20) solution = W g

$$\therefore \text{Strength of oxalic acid} = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{0.7875} (\text{N}/20) = S(\text{N})$$

(ii) 25 ml S(N) oxalic acid = V_{st} ml KMnO_4 solution

$$\therefore \text{Strength of } \text{KMnO}_4 = \frac{25 \times S}{V_{\text{st}}} (\text{N}) = \frac{25}{V_{\text{st}}} \times \frac{W}{0.7875 \times 20} (\text{N}) = 1.5873 \times \frac{W}{V_{\text{st}}} (\text{N}) = f(\text{N})$$

(iii) 25 ml Mohr's salt solution = V_1 ml $f(\text{N})$ KMnO_4 solution

$$\therefore 50 \text{ ml Mohr's salt solution} = 2V_1 \text{ ml } f(\text{N}) \text{ } \text{KMnO}_4 \text{ solution}$$

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(iv) For titration of 25 ml Fe^{3+} sample solution after reduction, the volume of KMnO_4 of strength $f(\text{N})$ required = V_{Fe} ml

$$1000 \text{ ml of (N) } \text{KMnO}_4 \equiv 55.85 \text{ g } \text{Fe}^{3+}$$

$$V_{\text{Fe}} \text{ ml } f(\text{N}) \text{ } \text{KMnO}_4 \text{ solution} = 0.05585 \times V_{\text{Fe}} \times f \text{ g } \text{Fe}^{3+}$$

$$25 \text{ ml supplied solution contains} = (0.05585 \times V_{\text{Fe}} \times f) \text{ g } \text{Fe}^{3+}$$

$$\therefore 1000 \text{ ml supplied solution contains} = (0.05585 \times V_{\text{Fe}} \times f \times 40) \text{ g } \text{Fe}^{3+}$$

$$= 0.05585 \times 40 \times V_{\text{Fe}} \times 1.5873 \times \frac{W}{V_{\text{st}}} \text{ g } \text{Fe}^{3+}$$

$$= 3.546 \times W \times \frac{V_{\text{Fe}}}{V_{\text{st}}} \text{ g } \text{Fe}^{3+}$$

$$\therefore \text{Therefore, the amount } \text{Fe}^{3+} \text{ iron present in supplied solution} = 3.546 \times W \times \frac{V_{\text{Fe}}}{V_{\text{st}}} \text{ g/L}$$

(v) For back titration of excess Mohr's salt solution, the volume of standard KMnO_4 of strength $f(\text{N})$ required = V_2 ml.

Therefore we may write, the amount of MnO_2 coming from the reaction + V_2 ml $f(\text{N})$ KMnO_4 solution \equiv 50 ml Mohr's salt solution $\equiv 2V_1$ ml $f(\text{N})$ KMnO_4 .

$$\therefore \text{The amount of } \text{MnO}_2 \text{ coming from the reaction} \equiv (2V_1 - V_2) \text{ ml } f(\text{N}) \text{ } \text{KMnO}_4 \text{ solution}$$

$$1000 \text{ ml (N) } \text{KMnO}_4 = 27.47 \text{ g } \text{Mn}^{2+}$$

$$\therefore (2V_1 - V_2) \text{ ml } f(\text{N}) \text{ } \text{KMnO}_4 = 0.02747 \times (2V_1 - V_2) \times f \text{ g } \text{Mn}^{2+}$$

$$25 \text{ ml supplied solution contains} = 0.02747 \times (2V_1 - V_2) \times f \text{ g } \text{Mn}^{2+}$$

$$\therefore 1000 \text{ ml supplied solution contains} = 0.02747 \times (2V_1 - V_2) \times f \times 40 \text{ g } \text{Mn}^{2+}$$

$$= 0.02747 \times 40 \times (2V_1 - V_2) \times 1.5873 \times \frac{W}{V_{\text{st}}} \text{ g } \text{Mn}^{2+}$$

$$= 1.744125 \times W \times \frac{2V_1 - V_2}{V_{\text{st}}} \text{ g } \text{Mn}^{2+}$$

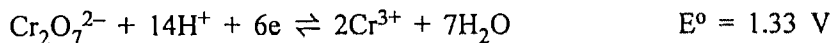
$$\therefore \text{The amount of } \text{Mn}^{2+} \text{ present in supplied solution} = 1.744125 \times W \times \frac{2V_1 - V_2}{V_{\text{st}}} \text{ g/L}$$

Dichromatometric Titration

3.1. General Discussion :

Redox titration conducting with the use of potassium dichromate solution is called Dichromatometric titrations or Dichromatometry. In acid medium, $\text{K}_2\text{Cr}_2\text{O}_7$ acts as a strong oxidant due to having high standard reduction potential (E^0).

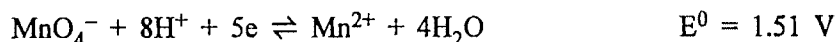
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Therefore, the equivalent weight is = Molecular weight/6 = $294.22/6 = 49.037$

It is obtained in form of pure orange crystals, thermally stable up to its fusion point and is highly soluble in water to form a stable orange coloured solution. Its strength remains unaltered for a long period of time and therefore serves as a primary standard solution.

The standard reduction potential of KMnO_4 in acid medium is equal to 1.51V which is higher than that of $\text{K}_2\text{Cr}_2\text{O}_7$ (1.33 V) indicates that the former is stronger oxidant than latter.



But the use of $\text{K}_2\text{Cr}_2\text{O}_7$ is more advantageous over KMnO_4 due to the following reasons:

- (i) $\text{K}_2\text{Cr}_2\text{O}_7$ is obtained in a very pure state.
- (ii) Aqueous solution of KMnO_4 is unstable towards light, heat, organic matters and also to its own component Mn^{2+} ion etc. to form MnO_2 . Again MnO_2 also catalyzes the decomposition of KMnO_4 . But $\text{K}_2\text{Cr}_2\text{O}_7$ solution is very stable and its strength remains unchanged for a long time.
- (iii) $\text{K}_2\text{Cr}_2\text{O}_7$ solution does not react with Cl^- , but KMnO_4 solution reacts. So Fe^{2+} or Fe^{3+} iron may be estimated by the use of $\text{K}_2\text{Cr}_2\text{O}_7$ solution directly in presence of Cl^- , but not by KMnO_4 solution. Thus, a standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$ is more useful and favourable oxidant than KMnO_4 solution.

Dichromatometric titration needs indicator to identify the equivalence point. Commonly used indicators are (i) Diphenylamine (ii) Sodium or Barium diphenylamine sulphonate (BDS). (iii) N-phenylanthranilic acid (iv) 5, 6 dimethyl ferroin etc. Mostly used indicator is the BDS indicator which gives a sharp colour change from colourless through green-violet to red-violet at the equivalence point. Its mechanism of functioning is discussed earlier. In estimation of Fe^{2+} by $\text{K}_2\text{Cr}_2\text{O}_7$ with the use of BDS or diphenylamine indicator, H_3PO_4 or NH_4HF_2 as complexing agent must be added prior to start of the titration to lower the reduction potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system. But if N-phenylanthranilic acid or ferroin as indicator is used, there is no need of addition of H_3PO_4 or NH_4HF_2 (see earlier).

3.2. Specifications :

A. Preparation of BDS indicator :

The solubility of BDS is not enough in water. So by boiling 0.5g BDS with 2g Na_2SO_4 in 100 ml water for 5 minutes and then filtering the cold solution, we can prepare more effective BDS solution used as redox indicator.

B. Preparation of a standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution :

For 250 ml (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution weight of solid $\text{K}_2\text{Cr}_2\text{O}_7$ required = $\frac{49.037}{4 \times 20} \text{ g} = 0.61296 \text{ g}$.

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An accurate weight nearly to the required weight (0.61296 g) is carefully taken into the funnel fitted to the neck of a 250 ml measuring flask. The solid is washed down completely by adding distilled water, flask is shaken to dissolve the solid into the solution, and finally the volume is made up to the mark of volumetric flask by drop wise addition of water with a jet dropper. The flask is stoppered, shaken to make the solution uniform.

Let, the weight of $K_2Cr_2O_7$ accurately transferred to the volumetric flask = W g

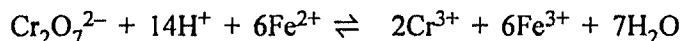
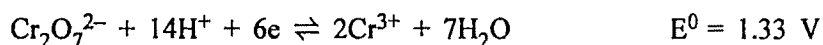
The strength factor of prepared standard $K_2Cr_2O_7$ solution (f) = weight taken/weight to be taken = $W/0.61296$ (N/20).

C. Use of standard $K_2Cr_2O_7$ solution :

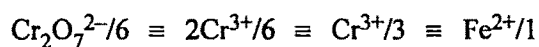
(i) Estimation of Ferrous iron in Mohr's salt (Standardization of Mohr's salt solution):

Theory :

In acid medium $K_2Cr_2O_7$ oxidises Fe^{2+} quantitatively to Fe^{3+}



In presence of H_3PO_4 or NH_4HF_2 that lowers the standard reduction potential of Fe^{3+}/Fe^{2+} system and makes suitable for the titration if BDS or diphenylamine indicator is used in the titration. Colour change is very sharp from green to red-violet.



$$\therefore 1000\text{ml of (N) } K_2Cr_2O_7 \equiv 55.85 \text{ g } Fe^{2+}$$

Chemicals required :

(i) Standard (N/20) $K_2Cr_2O_7$ solution, (ii) 2(N) H_2SO_4 solution, (iii) Syrupy H_3PO_4 acid or solid NH_4HF_2 , (iv) (N/20) Mohr's salt solution : ~ 5 g of Mohr's salt per 250 ml in 2(N) H_2SO_4 , (v) BDS indicator.

Procedure :

25 ml of the supplied solution of Fe^{2+} is pipetted out in a 250 ml conical flask. 100 ml 2(N) H_2SO_4 , 5ml syrupy H_3PO_4 and 4-6 drops of BDS indicator are added. The mixture is titrated with standard $K_2Cr_2O_7$ solution running from the burette with constant shaking until the first sharp red-violet colour is appeared indicating end point. The titration is repeated to get concordant results.

Experimental Data :

No. of titrations	Vol. of Mohr's salt solution taken (ml)	Burette reading of standard $K_2Cr_2O_7$ solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

Calculations :

Let, (i) W g of $K_2Cr_2O_7$ is accurately weighted and transferred to 250 ml volumetric flask to prepare a (N/20) solution.

$$\therefore \text{Strength of } K_2Cr_2O_7 = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{0.61296} \left(\frac{N}{20} \right) = \frac{W}{0.61296 \times 20} (N) = f(N)$$

(ii) Standard $K_2Cr_2O_7$ solution required for 25 ml of supplied Mohr's salt solution in titration = V_{st} ml

$$\begin{aligned} \therefore \text{Strength of Mohr's salt solution} &= \frac{V_{st} \times f}{25} (N) = \frac{V_{st}}{25} \times \frac{W}{0.61296 \times 20} (N) \\ &= 0.00326285 \times V_{st} \times W (N) \end{aligned}$$

$$1000\text{ml of } (N) K_2Cr_2O_7 \equiv 55.85 \text{ g } Fe^{2+}$$

$$V_{st} \text{ ml } f (N) K_2Cr_2O_7 = (0.05585 \times V_{st} \times f) \text{ g } Fe^{2+}$$

$$25 \text{ ml Mohr's salt contain} = (0.05585 \times V_{st} \times f) \text{ g } Fe^{2+}$$

$$\begin{aligned} \therefore 1000 \text{ ml Mohr's salt solution contain} &= (0.05585 \times 40 \times V_{st} \times f) \text{ g } Fe^{2+} \\ &= (2.234 \times V_{st} \times f) \text{ g } Fe^{2+} \end{aligned}$$

$$\text{Therefore, } Fe^{2+} \text{ iron present in Mohr's salt solution} = (2.234 \times V_{st} \times f) \text{ g/L.}$$

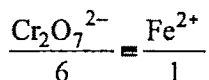
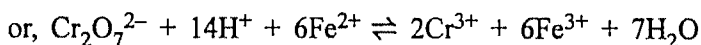
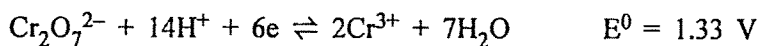
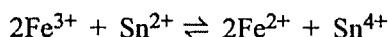
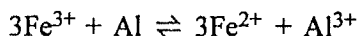
$$\begin{aligned} &= 2.234 \times V_{st} \times \frac{W}{0.61296 \times 20} \text{ g/L} \\ &= 0.18223 \times W \times V_{st} \text{ g/L} \end{aligned}$$

(ii) Estimation of Ferric iron in Ferric Salt :**Theory :**

At first Fe^{3+} ion in strong HCl medium is reduced to Fe^{2+} by Al-foil or by $SnCl_2$ (excess

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Sn^{2+} is neutralized by HgCl_2) and then the reduced Fe^{2+} is titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution in presence of H_3PO_4 or NH_4HF_2 using BDS or diphenylamine as indicator.



$$\therefore 1000\text{ml (N)} \text{ K}_2\text{Cr}_2\text{O}_7 \equiv 55.85 \text{ g Fe}^{3+}$$

Chemical required :

(a) For Fe^{3+} (~N/20) solution : As discussed earlier in Fe^{3+} vs. MnO_4^- titration.

(b) Other chemicals: As discussed earlier

Procedure :

25 ml supplied Fe^{3+} salt solution is pipetted out into a 500 ml conical flask, 30 ml conc. HCl is added and then the flask is heated to $80-90^\circ\text{C}$ on a wire gauge/asbestos board. The hot Fe^{3+} solution is reduced by introducing small Al -foils step by step with swirling until the yellow colour of Fe^{3+} solution just discharge with the formation of a clear solution through boiling. 100 ml distilled water is added immediately and cooled the flask to room temperature rapidly under the tap water. 5 ml H_3PO_4 or 2 g NH_4HF_2 , 4-6 drops of Barium diphenylamine sulphonate (BDS) indicator/diphenylamine indicator is added and the mixture is titrated rapidly with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution running from the burette until the first permanent red-violet colour appears which indicates the end point of the titration. The titration is repeated to get concordant results.

Results : Table as earlier.

Calculations : Same as in Fe^{2+} iron earlier.

(iii) Estimation of Ferrous and Ferric iron in a Mixture:

For Fe^{2+} :

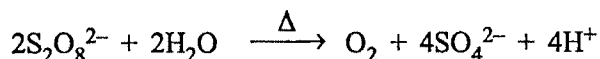
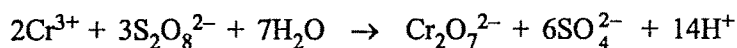
Fe^{2+} in presence of Fe^{3+} may easily be titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution directly by taking 25 ml aliquot of the supplied solution and following the procedure as Mohr's salt titration earlier dichromatometrically. The volume of $\text{K}_2\text{Cr}_2\text{O}_7$ obtained from the titration corresponds to the amount of Fe^{2+} ion present in 25 ml aliquot of the mixture.

For Fe^{3+} :

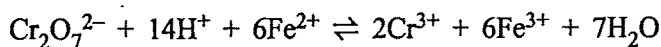
Fe^{3+} iron does not react with $\text{K}_2\text{Cr}_2\text{O}_7$, so it may be estimated indirectly as: 25 ml of the aliquot of the mixture of Fe^{2+} and Fe^{3+} is reduced first with Al-foil/ SnCl_2 solution in hot HCl medium and the total Fe^{2+} iron content of the mixture is titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution as discussed earlier. The titre value corresponds to total ($\text{Fe}^{2+} + \text{Fe}^{3+}$) present in 25 ml of the aliquot. Subtracting the amount of Fe^{2+} from the total amount of ($\text{Fe}^{3+} + \text{Fe}^{2+}$) ion, the amount of Fe^{3+} can be obtained. The detail procedure, results, calculations etc. are similar as earlier.

(iv) Estimation of Cr^{3+} in Chromic Salt:**Method 1 :****Theory :**

At first Cr^{3+} is oxidized to $\text{Cr}_2\text{O}_7^{2-}$ in H_2SO_4 medium by boiling with excess persulphate ($\text{S}_2\text{O}_8^{2-}$) solution in presence of a little AgNO_3 solution acting as catalyst. The excess persulphate remaining after the oxidation is completely destroyed by boiling the solution for a short time.



The amount of $\text{Cr}_2\text{O}_7^{2-}$ produced is then estimated by adding measured excess of standard Mohr's salt solution and then back titrating the excess Mohr's salt with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution using BDS indicator.



$$1000 \text{ ml (N) } \text{K}_2\text{Cr}_2\text{O}_7 = 17.34 \text{ g } \text{Cr}^{3+}$$

Chemicals required :**(a) For Cr^{3+} salt solution :**

1. For $\text{Cr}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$: 1.1 g salt is to be dissolved in 250 ml water and
2. for $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$: 2.1 g salt is to be dissolved in 250 ml water to prepare the supplied solution.

(b) For 1.5% AgNO_3 solution : 1.5 g AgNO_3 is to be dissolved in 100 ml distilled water.

(c) For 10% $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution: 10 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ salt to be dissolved in 100 ml water.

(d) Other chemicals: As usual.

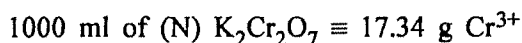
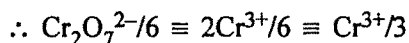
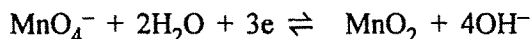
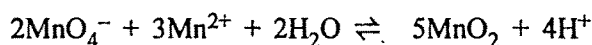
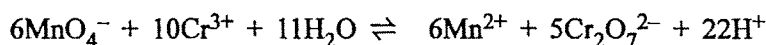
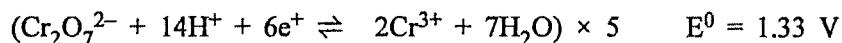
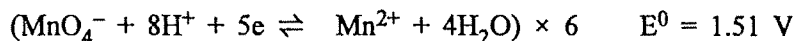
Procedure : 25 ml of the supplied Cr^{3+} solution is pipetted out in a 500 ml conical flask. 10 ml 1.5% AgNO_3 , 20 ml 10% $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution and 5ml conc. H_2SO_4 are added carefully.

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A funnel is placed over the mouth of the conical flask and is boiled gently for 20 minutes. 50 ml distilled water is added and the flask is cooled under tap water. Then a measured excess (say 2×25 ml) of standard Mohr's salt solution is added with the help of a pipette. 5 ml H_3PO_4 or 2 g NH_4HF_2 and 4-6 drops BDS indicator are added. The excess Mohr's salt solution of the final mixture is then back titrated with a standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$ as usual.

Method 2 :

Theory : Cr^{3+} may be oxidized to $\text{Cr}_2\text{O}_7^{2-}$ quantitatively in H_2SO_4 medium by boiling with excess KMnO_4 solution. Then the produced insoluble MnO_2 is removed by filtration and remaining excess KMnO_4 in the filtrate is decomposed by conc. HCl through boiling to expel Cl_2 . The fresh orange solution of $\text{Cr}_2\text{O}_7^{2-}$ is then mixed with measured excess standard Mohr's salt solution. After reaction the excess Mohr's salt solution is back titrated with a standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution using $\text{H}_3\text{PO}_4/\text{NH}_4\text{HF}_2$ and BDS as indicator.



Chemicals required :

- (a) For Cr^{3+} salt solution: As discussed earlier
- (b) For KMnO_4 (N/10) solution: As described earlier.
- (c) Other chemicals: As usual.

Procedure :

25 ml of Cr^{3+} solution is pipetted out in a 500 ml beaker and is kept covered with a watch glass. 50 ml of 8(N) H_2SO_4 and 60 ml approximately (N/10) KMnO_4 solution are added. The beaker is placed on a wire gauge and the solution is boiled gently and carefully for 40 minutes with occasional stirring with a glass rod. Water is added to replenish the loss by boiling and to ensure excess, more KMnO_4 solution is added if required (seen by KMnO_4 colour). After cooling the pink/brown coloured solution is filtered carefully into a 500 ml beaker using ordinary filter paper. The beaker and the filter paper with precipitate is washed thoroughly and quantitatively by taking 50 ml hot distilled water using 5 ml portion each time through spraying

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with the help of a fine jet mouth dropper. The filtrate with washing is boiled for 30 minutes by adding minimum drops of conc. HCl till pink colour of MnO_4^- is discharged with concomitant complete removal of dissolved Cl_2 . Then the fresh orange $\text{Cr}_2\text{O}_7^{2-}$ solution is cooled to room temperature under tap water. 50 ml (measured excess) Mohr's salt solution is added by means of a pipette carefully. 5 ml H_3PO_4 or 2 g NH_4HF_2 and 4-6 drops of BDS indicator are added. The excess Mohr's salt solution of the final mixture is then back titrated with a standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution as usual.

Experimental Data : Table as earlier.

Calculation :

Let,

- (i) W g of $\text{K}_2\text{Cr}_2\text{O}_7$ is accurately weighed and transferred to 250 ml volumetric flask to prepare a (N/20) solution.

$$\therefore \text{Strength of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{0.61296} \left(\frac{N}{20} \right) = \frac{W}{0.61296 \times 20} (N) = f(N)$$

- (ii) For standardization of 25 ml Mohr's salt solution, the volume of standard dichromate of strength f(N) required = V_1 ml

$$\therefore 50 \text{ ml Mohr's salt solution} = 2V_1 \text{ ml } f(N) \text{ } \text{K}_2\text{Cr}_2\text{O}_7 \text{ solution}$$

- (iii) For back titration of excess Mohr's salt solution, standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution of strength f(N) required = V_2 ml.

Therefore, we may write, the amount of $\text{Cr}_2\text{O}_7^{2-}$ of the reaction mixture + V_2 ml f(N) $\text{K}_2\text{Cr}_2\text{O}_7$ solution \equiv 50 ml Mohr's salt solution $\equiv 2V_1$ ml f (N) $\text{K}_2\text{Cr}_2\text{O}_7$.

$$\therefore \text{The amount of } \text{Cr}_2\text{O}_7^{2-} \text{ of the reaction mixture} \equiv (2V_1 - V_2) \text{ ml } f(N) \text{ } \text{K}_2\text{Cr}_2\text{O}_7 \text{ solution}$$

$$1000 \text{ ml } (N) \text{ } \text{K}_2\text{Cr}_2\text{O}_7 = 17.34 \text{ g } \text{Cr}^{3+}$$

$$\therefore (2V_1 - V_2) \text{ ml } f(N) \text{ } \text{K}_2\text{Cr}_2\text{O}_7 = 0.01734 \times (2V_1 - V_2) \times f \text{ g } \text{Cr}^{3+}$$

$$25 \text{ ml supplied } \text{Cr}^{3+} \text{ solution contains} = 0.01734 \times (2V_1 - V_2) \times f \text{ g } \text{Cr}^{3+}$$

$$\therefore 1000 \text{ ml supplied solution contains} = 0.01734 \times 40 \times (2V_1 - V_2) \times f \text{ g } \text{Cr}^{3+}$$

$$= 0.01734 \times 40 \times (2V_1 - V_2) \times \frac{W}{0.61296 \times 20} \text{ g } \text{Cr}^{3+}$$

$$= 0.056578 \times W \times (2V_1 - V_2) \text{ g } \text{Cr}^{3+}$$

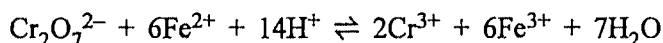
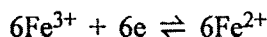
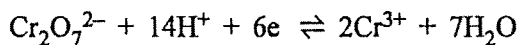
$$\therefore \text{Cr}^{3+} \text{ present in supplied solution} = 0.056578 \times W \times (2V_1 - V_2) \text{ g/L}$$

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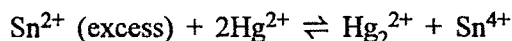
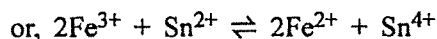
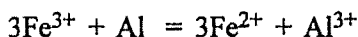
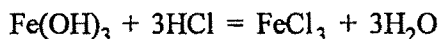
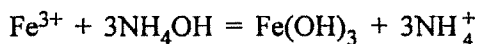
(v) Estimation of Cr^{6+} ($\text{Cr}_2\text{O}_7^{2-}$) and Fe^{3+} in a mixture:

Theory :

$\text{Cr}_2\text{O}_7^{2-}$ can be estimated in 2(N) H_2SO_4 acid medium directly by mixing with measured excess of standard Mohr's salt solution and then back titrating the excess Mohr's salt solution with syrupy H_3PO_4 or NH_4HF_2 and BDS indicator. Fe^{3+} does not interfere under this condition.



For estimation of Fe^{3+} , it is separated from $\text{Cr}_2\text{O}_7^{2-}$ by precipitating as $\text{Fe}(\text{OH})_3$ using excess NH_4OH . The washed $\text{Fe}(\text{OH})_3$ is dissolved in 1:1 HCl and then reduced to Fe^{2+} by Al-foil or by SnCl_2 as usual. Finally Fe^{2+} is directly titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution using syrupy H_3PO_4 or NH_4HF_2 and BDS as indicator.



$$\begin{aligned} \therefore 1000 \text{ ml of (N) } \text{K}_2\text{Cr}_2\text{O}_7 &\equiv 1000 \text{ ml (N) Mohr's salt} \equiv 36 \text{ g of } \text{Cr}_2\text{O}_7^{2-} \\ &\equiv 17.34 \text{ g } \text{Cr}^{6+} \equiv 55.847 \text{ g of } \text{Fe}^{3+} \end{aligned}$$

Chemicals required :

- (a) For Cr^{3+} salt solution: As discussed earlier
- (b) For KMnO_4 (N/10) solution: As described earlier.
- (c) Other chemicals: As usual.

Procedure :

Estimation of Cr^{6+} ($\text{Cr}_2\text{O}_7^{2-}$) : 25 ml aliquot from the supplied solution is pipetted into a 250ml conical flask; then added successively 25 ml of 4(N) H_2SO_4 , 50 ml of the standard Mohr's salt solution by means of a pipette, 5 ml syrupy H_3PO_4 or 2 g of NH_4HF_2 and 4-6 drops of BDS indicator. The resulting mixture is titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution until the first reddish-violet colour appears. Titration is repeated to get concordant results.

Estimation of Fe^{3+} : 25 ml of the supplied solution is again pipetted out into a 500 ml beaker, diluted with 50 ml distilled water and then 1:1 aqueous NH_3 solution is added drop wise with stirring by a glass rod until a permanent strong smell of NH_3 persists. The mixture is digested without boiling on a low flame for 5 minutes. The solution is then cooled and filtered through Whatman 41 filter paper. The beaker and the filter paper containing $\text{Fe}(\text{OH})_3$ is washed thoroughly by 0.1% NH_4Cl solution containing little NH_3 taking 5 ml each time through spraying with the help of a fine jet mouth dropper. Then the washed precipitate of $\text{Fe}(\text{OH})_3$ is dissolved into the same original beaker and the filter paper is washed free from any yellow stain step by step by using alternatively a total of 50 ml hot 9(N) HCl and 20 ml hot distilled water. The solution is heated near to boiling and a few pieces of Al-foils is introduced with constant stirring until the reduction of $\text{Fe}(\text{III})$ ion is complete with the formation of a clear solution through boiling. 100 ml distilled water is added immediately and the beaker is cooled to room temperature rapidly under the tap water carefully. 5 ml H_3PO_4 or 2 g of NH_4HF_2 and 4-6 drops of BDS indicator are added and the mixture is titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution as usual.

Experimental data : Table as earlier for Cr^{3+} and Fe^{3+} .

Calculation :

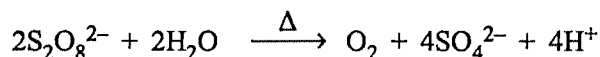
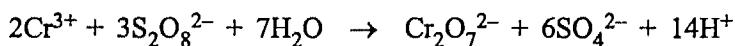
(a) For Cr^{6+} : Same as Cr^{3+} estimation earlier.

(b) For Fe^{3+} : Same as estimation of Fe^{3+} in ferric salt earlier.

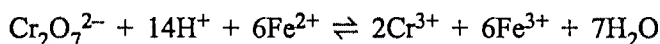
(vi) Estimation of Cr^{3+} and Fe^{3+} in a mixture :

Theory :

At first Cr^{3+} is oxidized to $\text{Cr}_2\text{O}_7^{2-}$ in H_2SO_4 medium by boiling with excess $\text{S}_2\text{O}_8^{2-}$ solution in presence of a little AgNO_3 solution acting as catalyst. The excess $\text{S}_2\text{O}_8^{2-}$ remaining after the oxidation is completely destroyed by boiling the solution for a short time.



The $\text{Cr}_2\text{O}_7^{2-}$ produced in the reaction is then estimated by adding measured excess volume of standard Mohr's salt solution and then back titrating the excess Mohr's salt solution with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution using BDS indicator.



In this situation Fe^{3+} present in supplied mixture does not react and interfere in estimation of Cr^{3+} .

For estimation of Fe^{3+} ion, the mixture is treated with excess $\text{S}_2\text{O}_8^{2-}$ in presence of AgNO_3

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solution to oxidize Cr^{3+} to $\text{Cr}_2\text{O}_7^{2-}$ and then solution is made ammoniacal with excess (1:1) NH_3 to precipitate Fe^{3+} as $\text{Fe}(\text{OH})_3$. It is then filtered, washed, dissolved in (1:1) HCl and is reduced to Fe^{2+} by Al foil in hot condition. Finally the solution containing Fe^{2+} is titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution using $\text{H}_3\text{PO}_4 / \text{NH}_4\text{HF}_2$ and BDS as indicator. Reactions are same.

\therefore 1000 ml of (N) $\text{K}_2\text{Cr}_2\text{O}_7 \equiv$ 1000 ml (N) Mohr's salt \equiv 17.34 g $\text{Cr}^{3+} \equiv$ 55.847 g of Fe^{3+}

Chemicals required :

- (a) For Cr^{3+} salt solution: As discussed earlier
- (b) For KMnO_4 (N/10) solution: As described earlier.
- (c) Other chemicals: As usual.

Procedure :

(a) Estimation of Cr^{3+} :

Same as estimation of Cr^{3+} in chromic salt.

(b) Estimation of Fe^{3+} :

25 ml of the supplied solution is again pipetted out into a 500 ml beaker. 10 ml 1.5% AgNO_3 , 20 ml 10% $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution and 5 ml conc. H_2SO_4 are added with stirring by a glass rod carefully. The solution of the beaker is gently boiled for 20 minutes by keeping the beaker covered with a watch glass. 50 ml water and then 1:1 aqueous NH_3 is added to the hot solution drop wise with stirring till the solution is strongly ammoniacal. The mixture is cooled to settle down the $\text{Fe}(\text{OH})_3$ as precipitate. It is filtered through Whatman No. 41 filter paper. The beaker and the filter paper is washed thoroughly with 50 ml 0.1% NH_4Cl solution containing little NH_3 taking 5 ml portion each time through spraying with the help of a fine jet mouth dropper. Then the precipitate is dissolved into the same original beaker and the filter paper is washed free from any yellow stain step by step by using alternatively a total of 50 ml hot 9(N) HCl and 20 ml hot distilled water. The solution is heated near to boiling and a few pieces of Al -foils is introduced with constant stirring until the reduction of $\text{Fe}(\text{III})$ ion is complete with the formation of a clear solution through boiling. 100 ml distilled water is added immediately and the beaker is cooled to room temperature rapidly under the tap water carefully. 5 ml H_3PO_4 or 2 g of NH_4HF_2 , 4-6 drops of BDS indicator are added and the mixture is titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution as usual.

Experimental data: Table as earlier.

Calculation : As earlier.

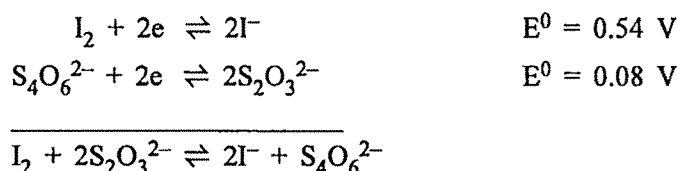
Iodimetry and Iodometry

4.1. General Discussion :

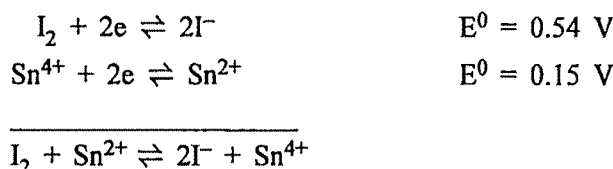
The term "iodimetry" expresses the use of standard solution of iodine as an oxidant in titrations to estimate the amount of other components acting as reductants. On the other hand, "Iodometry" explains the titration of iodine liberated in chemical reactions from iodide which acts as a reductant. The reactions help to estimate the amount of oxidants through the quantitative liberation of iodine. As for examples:

(a) Iodimetry :

(i) Estimation of $S_2O_3^{2-}$: The reactions:

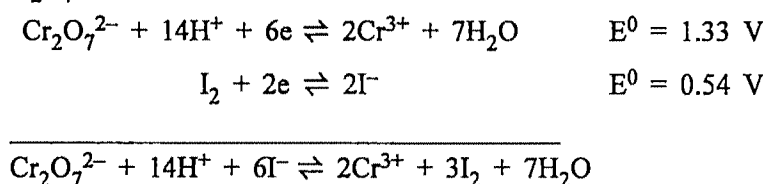


(ii) Estimation of Sn^{2+} : The reactions

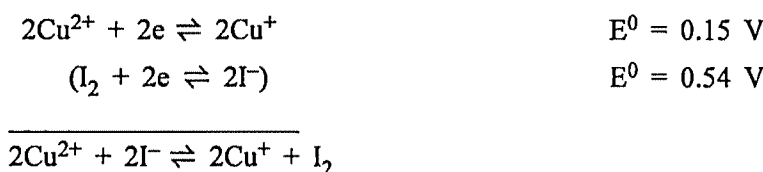


(b) Iodometry :

(i) Estimation of $Cr_2O_7^{2-}$: The reactions:

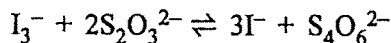


(ii) Estimation of Cu^{2+} :

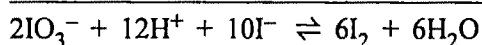
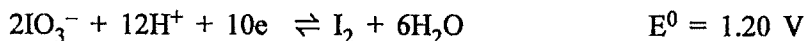


Solid I_2 is less soluble in water but considerably soluble in a solution of iodide due to formation of I_3^- . ($I_2 + I^- \rightleftharpoons I_3^-$). So, in iodimetric or iodometric titration sufficient amount of KI is used to increase the solubility of I_2 by shifting the point of above equilibrium to the right direction.

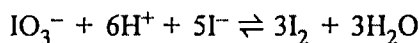
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A standard iodine solution may be prepared by dissolving an accurate weight of pure KIO_3 in a definite volume of solution containing a slight excess of required pure KI . On acidification the solution will produce I_2 readily equivalent to that of amount of IO_3^- present into the solution by the following reactions :

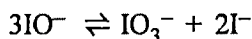
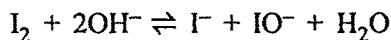


or,

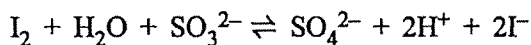
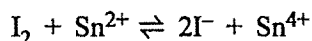
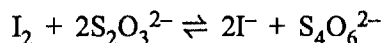


This standard solution of KIO_3 and KI is stable enough and may be kept for a long time as a source of known quantity of iodine. Although another source of a secondary solution of I_2 solution is prepared directly by dissolving a rough weight of required I_2 in excess KI solution and thus needs standardization.

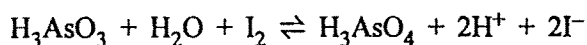
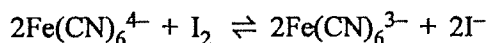
The standard reduction potential of $\text{I}_2/2\text{I}^-$ system is independent of pH. But at higher pH (i.e., alkaline medium) I_2 reacts with OH^- to form I^- and unstable IO^- which disproportionate to I^- and IO_3^- immediately.



As a result, iodimetric or iodometric titrations should not be carried out at sufficiently alkaline medium (pH 8). Strong reducing agents having much lower reduction potential than that of $\text{I}_2/2\text{I}^-$ system, such as $\text{S}_2\text{O}_3^{2-}$, Sn^{2+} , SO_3^{2-} , S^{2-} etc react rapidly and quantitatively with I_2 even in acid medium.



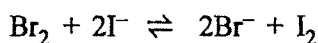
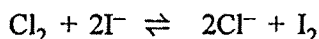
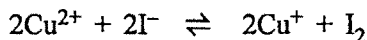
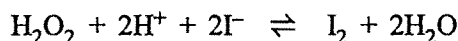
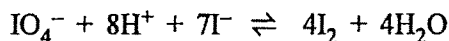
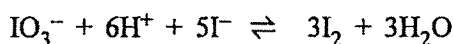
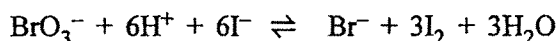
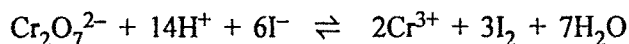
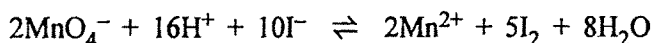
Weaker reducing agents such as As^{3+} , Sb^{3+} , $\text{Fe}(\text{CN})_6^{4-}$ etc. show a complete reaction with I_2 (Iodimetric reaction) at pH range 4 to 8, where the reduction potential of the systems are lowest, i.e., reducing power is maximum. The following reactions occur:



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But in strongly acid medium ($\text{pH} < 2$) the reduction potential exceeds the potential of $\text{I}_2/2\text{I}^-$ system, the reverse reactions from left to right (Iodometric reactions) with the quantitative liberation of I_2 take place which is discussed earlier.

The strong oxidizing agents in neutral or acid medium react with excess I^- to liberate equivalent amount of I_2 that may be estimated by standard thiosulphate solution. Examples are :



There are mainly two sources of error in titrations involving iodine.

(i) loss of I_2 due to its considerable volatility, (ii) aerial oxidation of I^- to I_2 in acid solution. Loss due to volatility is minimized (i) through the trapping of I_2 by I^- to I_3^- (ii) by carrying the reaction in cold. Aerial oxidation may be minimized by displacing air of the conical flask by CO_2 (i.e., adding 0.2 g NaHCO_3) and by performing titration rapidly.

Use of indicator

An aqueous solution of starch is used as the suitable indicator in iodimetric or iodometric titrations. Starch is a polysaccharide having glucose units in skeleton. Glucose units of starch react with I_2 to form an intense blue coloured unstable complex, which is visible at a very low concentration of I_2 . During titration when the titrating mixture exhibits straw yellow colour of I_2 , then starch is added. On shaking it develops deep blue coloured solution. Gradual addition of $\text{S}_2\text{O}_3^{2-}$ which consumes I_2 completes the reaction by the just disappearance of the blue colour of the solution. Sodium starch glycollate which is superior to starch may be used in the same titration in place of starch.

4.2. Specifications :

A. Preparation of starch solution :

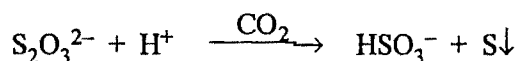
One gram soluble starch is mixed with water to obtain a thin paste like solution. It is then

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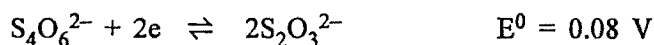
poured into 100 ml boiling water with stirring and the mixture is boiled until a clear solution is obtained. The cooled clear starch solution is stored in a stoppered bottle. Starch solution is unstable in nature and is affected by bacteria, fungus etc. It hydrolyses in strong acid solution. 2-3 ml of freshly prepared starch solution should be used in each titration.

B. Preparation of $\text{Na}_2\text{S}_2\text{O}_3$ solution :

Sodium thiosulphate (hypo) is available in crystalline form as $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. It is efflorescent in nature and so it is not a primary standard substance. The aqueous solution is unstable due to decomposition by the acidic function of aerial CO_2 , bright sunlight or by bacteria.



It acts as a weak reducing agent due to its low reduction potential and reduces I_2 to I^- rapidly and itself oxidizes to tetrathionate.



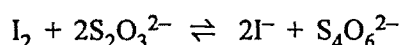
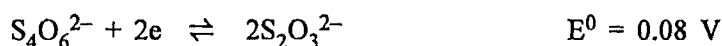
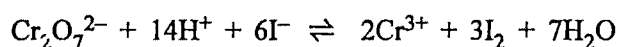
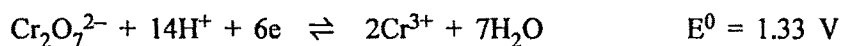
Therefore, equivalent weight of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ($M = 248$) = Mol wt / 1 = 248

To prepare a 250 ml 0.05(N) $\text{Na}_2\text{S}_2\text{O}_3$ solution, wt to be taken = $248 \times 250 / 1000 \times 20\text{g} = 3.1 \text{ g}$.

The thiosulphate solution prepared by direct weighing is thus a secondary standard and needs standardization each time before or after use. 3 drops CHCl_3 or 0.1 g Na_2CO_3 per litre of solution may be used to protect the solution for a few days.

C. Standardization of sodium thiosulphate solution

$\text{Na}_2\text{S}_2\text{O}_3$ solution may be standardized iodometrically by the use of standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution. In acid medium $\text{Cr}_2\text{O}_7^{2-}$ reacts with I^- to liberate equivalent amount of I_2 which is titrated with $\text{Na}_2\text{S}_2\text{O}_3$ solution using freshly prepared starch as indicator.



Procedure :

25 ml of standard $K_2Cr_2O_7$ solution is pipetted out into a 500 ml conical flask. 25 ml 4(N) H_2SO_4 and 10 ml of 20% KI solution added. The flask is covered with a watch glass and is kept in dark for 5 minutes. The watch glass and the inner wall of the flask are washed down with 150 ml distilled water. The mixture is titrated rapidly with $Na_2S_2O_3$ solution running from the burette until the brown colour fades to straw-yellow. 2 ml 1% freshly prepared starch solution is added, shaken to obtain the blue coloured solution. The titration is continued until the blue colour just disappears to a green solution by one drop of excess $Na_2S_2O_3$ solution that indicates the end point of the titration. The titration is repeated to get a concordant result.

Experimental Data :**Table : Standardization of $Na_2S_2O_3$ solution:**

No. of titrations	Vol. of $K_2Cr_2O_7$ solution taken (ml)	Burette reading of thiosulphate solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

Calculation :

Let, (i) An accurate wt of $K_2Cr_2O_7$ taken to prepare a 250 ml (N/20) solution = W g.

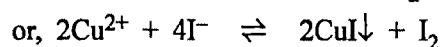
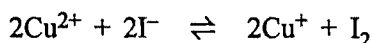
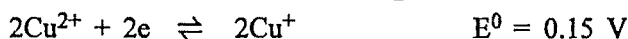
∴ The strength of $K_2Cr_2O_7$ solution = wt. taken/wt. to be taken = $W/0.61296$ (N/20) = $W/0.61296 \times 20(N) = f(N)$

(ii) For 25 ml standard $K_2Cr_2O_7$ solution of strength f(N), the volume of $Na_2S_2O_3$ solution required for standardization = V_{st} ml

∴ Strength of $Na_2S_2O_3$ solution (S_1) = $25 \times f/V_{st}(N) = 25/V_{st} \times W/0.61296 \times 20(N)$
 $= 2.039285 \times W/V_{st}(N)$

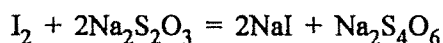
D. Use of standard thiosulphate solution :**(i) Estimation of copper in copper sulphate ($CuSO_4 \cdot 5H_2O$) solution :****Theory :**

In neutral or slightly acidic medium, Cu^{2+} ion liberates I_2 quantitatively from KI as:



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CuI is extremely insoluble ($K_{sp} = 1.1 \times 10^{-12}$), it gets precipitated. As a result, the concentration of Cu^+ in solution becomes very poor to increase the formal potential of $\text{Cu}^{2+}/\text{Cu}^+$ about 0.85 V (from $E^0 = 0.15\text{V}$). Consequently, the final reaction is spontaneous and quantitative. The liberated I_2 is then titrated with standard $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as indicator.



CuI may absorb a trace I_2 and that can be removed and titrated by the addition of NH_4SCN solution before the end point and continuing the titration upto the colour change.

$$\therefore 1000 \text{ ml (N) thio} = 63.546 \text{ g of Cu}^{2+}$$

Chemicals required :

- (a) CuSO_4 solution ($\sim\text{N}/20$): Dissolve 12.5 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (F.W. = 249.5) in 50 ml water + 5 ml C. H_2SO_4 , (b) Standard ($\text{N}/20$) $\text{K}_2\text{Cr}_2\text{O}_7$ solution, (c) $\sim(\text{N}/20)$ Thiosulphate solution, (d) 10% KI solution, (e) 1% Starch solution, (f) 20% NH_4SCN solution.

Procedure :

25 ml of the supplied Cu^{2+} salt solution is pipetted into a 250 ml conical flask and diluted to 50 ml with distilled water. $\text{NH}_3 : \text{H}_2\text{O}$ (1 : 2) solution is added drop wise with shaking until a bluish-white turbidity persists and dissolved the same by adding about 2 gms of NH_4HF_2 . 20 ml of 10% KI solution is added and the solution is titrated at once with standard ($\text{N}/20$) thiosulphate solution to obtain a straw-yellow colour. 2 ml 1% starch indicator is added and the titration is continued until a milky white precipitate appears. The titration is completed by addition of thiosulphate, in case a blue colour appears with the addition of 10 ml 20% NH_4SCN solution. Repeat the titration to get the concordant results.

Experimental data :

(a) Table as earlier for standardization of thio solution

(b) Table for estimation of Cu^{2+} :

No. of titrations	Vol. of Cu^{2+} solution taken (ml)	Burette reading of thiosulphate solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

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Calculation :

Let,

(i) an accurate wt of $K_2Cr_2O_7$ taken to prepare a 250 ml (N/20) solution = W g.

$$\therefore \text{Strength of } K_2Cr_2O_7 = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{0.61296} \left(\frac{N}{20} \right) = \frac{W}{0.61296 \times 20} (N) = f(N)$$

(ii) For 25 ml standard $K_2Cr_2O_7$ solution of strength f (N), the volume of $Na_2S_2O_3$ solution required for standardization = V_{st} ml

$$\begin{aligned} \therefore \text{Strength of } Na_2S_2O_3 \text{ solution}(S_1) &= \frac{25 \times f}{V_{st}} (N) = \frac{25}{V_{st}} \times \frac{W}{0.61296 \times 20} (N) \\ &= 2.039285 \times \frac{W}{V_{st}} (N) \end{aligned}$$

(iii) For estimation of 25 ml Cu^{2+} solution, the volume of standard thio of strength $S_1(N)$ required = V_{Cu} ml.

$$1000 \text{ ml (N) thio} = 63.546 \text{ g } Cu^{2+}$$

$$\therefore V_{Cu} \text{ ml } S_1(N) \text{ thio} = 0.063546 \times V_{Cu} \times S_1 \text{ g } Cu^{2+}$$

$$25 \text{ ml } Cu^{2+} \text{ solution contains} = 0.063546 \times V_{Cu} \times S_1 \text{ g } Cu^{2+}$$

$$\begin{aligned} \therefore 1000 \text{ ml } Cu^{2+} \text{ solution contains} &= 0.063546 \times 40 \times V_{Cu} \times 2.039285 \times \frac{W}{V_{st}} \text{ g } Cu^{2+} \\ &= 5.18354 \times W \times \frac{V_{Cu}}{V_{st}} \text{ g } Cu^{2+} \end{aligned}$$

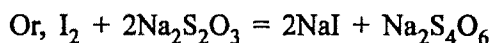
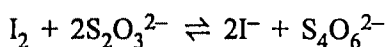
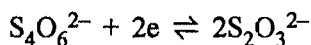
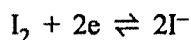
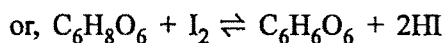
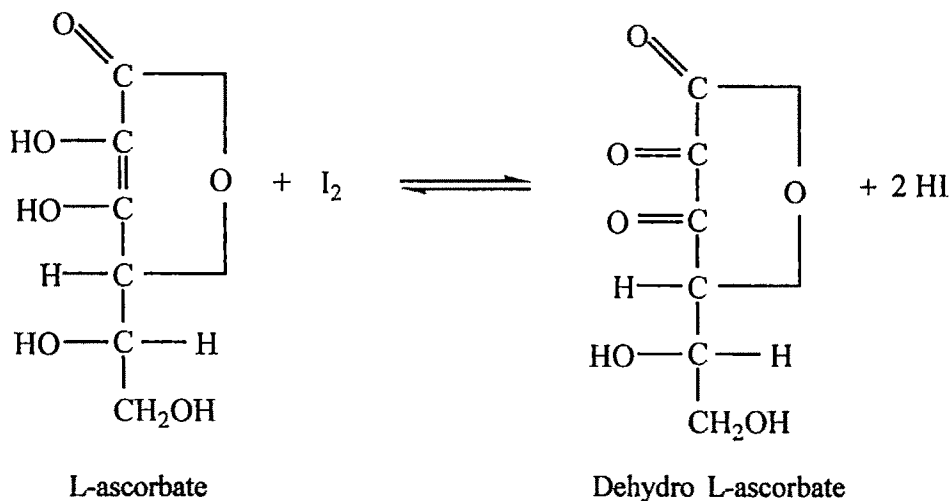
$$\text{Therefore, } Cu^{2+} \text{ present in supplied solution} = 5.18354 \times W \times \frac{V_{Cu}}{V_{st}} \text{ g/L}$$

Estimation of Vitamin C iodometrically :

Theory :

In nature ascorbic acid (Vitamin C) exists in the form of reduced L-ascorbate. In aqueous solution the L-ascorbate reduces iodine quantitatively to HI and itself oxidized to dehydro L-ascorbate. For estimation, a measured excess of standard I_2 solution is added to a given volume of L-ascorbate and then the excess I_2 is back titrated with a standard thiosulfate solution using freshly prepared starch solution as indicator.

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$$\therefore 1 \text{ mol } \text{C}_6\text{H}_8\text{O}_6 \equiv 1 \text{ mol } \text{I}_2 \equiv 2 \text{ moles } \text{Na}_2\text{S}_2\text{O}_3$$

$$\equiv 2 \times 1 \text{ mol of } \text{Na}_2\text{S}_2\text{O}_3 = 2 \times 1 \text{ equivalent of } \text{Na}_2\text{S}_2\text{O}_3$$

[As, equivalent wt of $\text{Na}_2\text{S}_2\text{O}_3 = 2 \times \text{Mole of } \text{Na}_2\text{S}_2\text{O}_3 / 2 = \text{Mol wt of } \text{Na}_2\text{S}_2\text{O}_3]$

$$\therefore \text{Equivalent wt of } \text{C}_6\text{H}_8\text{O}_6 = \text{mol wt of } \text{C}_6\text{H}_8\text{O}_6 / 2 = 176.12 / 2 = 88.06 \text{ g } \text{C}_6\text{H}_8\text{O}_6$$

$$\therefore 1000 \text{ ml (N) } \text{Na}_2\text{S}_2\text{O}_3 \text{ solution} \equiv 88.06 \text{ g } \text{C}_6\text{H}_8\text{O}_6$$

Chemicals required :

- (a) Ascorbic acid (Vit-C) solution (~N/20): Dissolve 4 g ascorbic acid in 1000 ml distilled water or Vitamin-C tablet or lemon juice may be supplied.
- (b) Standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution
- (c) ~N/20 sodium thiosulphate solution
- (d) 10% KI solution
- (e) 1% starch solution
- (f) ~N/20 I_2 solution in KI: (6 g solid I_2 + 20 g KI) dissolve step by step in fractions of 1000 ml distilled water.

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Procedure :

(a) Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution against Standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution: As discussed earlier.

(b) Standardization of iodine solution with Standard thiosulfate solution:

25 ml of the iodine solution is pipetted out in a 500 ml conical flask, diluted to 150 ml with distilled water and titrated with the standard $\text{Na}_2\text{S}_2\text{O}_3$ solution as discussed earlier.

(c) Estimation of supplied Vitamin-C solution :

25 ml of Vitamin-C solution is pipetted out into a 500 ml conical flask. 50 ml distilled water and 2 ml 2(N) H_2SO_4 are added. A measured excess of 50 ml of standard (N/20) iodine solution is added with the help of a pipette and then excess iodine is titrated rapidly with standard thiosulphate solution as usual. Repeat the titration to get concordant results.

Experimental data :

(a) Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ by Standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution :

No. of titrations	Vol. of standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution taken (ml)	Burette reading of thiosulphate solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

(b) A similar table for estimation of I_2 solution as above.

(c) Estimation of unknown Vitamin C solution :

No. of titrations	Volume of Vitamin C solution taken (ml)	Volume of I_2 solution taken (ml)	Burette reading of standard thiosulphate solution (ml)			
			Initial	Final	Difference	Most frequent reading
1	25	50	0			
2	25	50	0			
3	25	50	0			

Calculation :

Let,

(i) an accurate wt of $\text{K}_2\text{Cr}_2\text{O}_7$ taken to prepare a 250 ml (N/20) solution = W g.

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∴ Strength of $K_2Cr_2O_7$ solution = wt. taken/wt. to be taken = $W/0.61296 (N/20) = W/0.61296 \times 20 (N) = f(N)$

(ii) For 25 ml standard $K_2Cr_2O_7$ solution of strength $f(N)$, the volume of $Na_2S_2O_3$ solution required for standardization = V_{st} ml

∴ Strength of $Na_2S_2O_3$ solution (S_1) = $25 \times f/V_{st} (N) = 25/V_{st} \times W/0.61296 \times 20 (N) = 2.039285 \times W/V_{st} (N)$

(iii) For standardization of I_2 solution, the volume of standard $Na_2S_2O_3$ solution of strength $S_1(N)$ required for 25ml of I_2 solution = V_1 ml.

∴ 50 ml of I_2 solution = $2V_1$ ml $S_1(N)$ thio solution.

(iv) For back titration of excess I_2 solution, standard thio solution of strength $S_1(N)$ required = V_2 ml.

Therefore, we may write, the amount of ascorbic acid (Vitamin C) + V_2 ml $S_1(N)$ thio (for back titration) \equiv 50 ml I_2 solution \equiv $2V_1$ ml $S_1(N)$ thio solution

∴ The amount of ascorbic acid (Vitamin C) \equiv $(2V_1 - V_2)$ ml $S_1(N)$ thio

1000 ml (N) thio = 88.06 g $C_6H_8O_6$

∴ $(2V_1 - V_2)$ ml $S_1(N)$ thio = $0.08806 \times (2V_1 - V_2) \times S_1$ g $C_6H_8O_6$

25 ml supplied Vitamin C solution contains = $0.08806 \times (2V_1 - V_2) \times S_1$ g $C_6H_8O_6$

∴ 1000 ml supplied Vitamin C solution contains = $0.08806 \times 40 \times (2V_1 - V_2) \times 2.039285 \times W/V_{st}$ g $C_6H_8O_6$

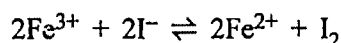
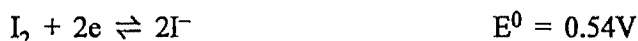
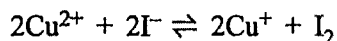
= $7.18318 \times W \times \frac{2V_1 - V_2}{V_{st}}$ g $C_6H_8O_6$

∴ Vitamin C present in solution = $7.18318 \times W \times \frac{2V_1 - V_2}{V_{st}}$ g / L

(iii) Estimation of Cu^{2+} and Fe^{3+} in a mixture :

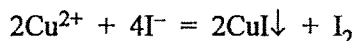
Theory:

Both Fe^{3+} and Cu^{2+} can react to produce I_2 from neutral or slightly acidic solution of KI.

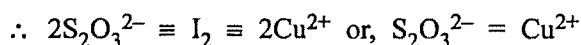
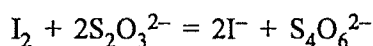


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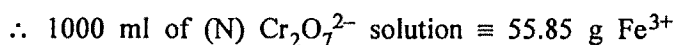
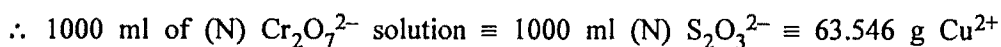
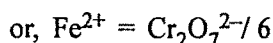
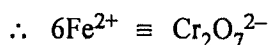
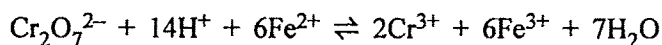
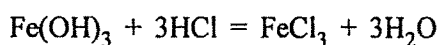
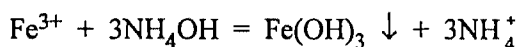
But in presence of excess NH_4HF_2 , Fe^{3+} forms FeF_6^{3-} complex, therefore the formal potential of $\text{Fe}^{3+} / \text{Fe}^{2+}$ system falls below the standard reduction potential of $\text{I}_2/2\text{I}^-$ system. As a result Fe^{3+} can no longer react I^- to produce I_2 . On the other hand, Cu^{2+} reacts I^- to produce I_2 , because cuprous iodide (CuI) which is extremely insoluble ($K_{\text{sp}} = 1.1 \times 10^{-12}$) to form precipitate:



and the formal potential of $\text{Cu}^{2+} / \text{Cu}^+$ system increases over the standard reduction potential of $\text{I}_2/2\text{I}^-$ system. Consequently Cu^{2+} liberates I_2 from I^- spontaneously and quantitatively. I_2 thus liberated only by Cu^{2+} is titrated with standard $\text{S}_2\text{O}_3^{2-}$ solution using starch as indicator.



For estimation of Fe^{3+} , it is first separated out from Cu^{2+} completely as $\text{Fe}(\text{OH})_3$ precipitate by treating with excess aqueous NH_3 . Then by dissolving the precipitate of $\text{Fe}(\text{OH})_3$ in HCl and reducing it by Al -foils, the produced Fe^{2+} is titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution using H_3PO_4 or NH_4HF_2 and BDS as indicator.



Chemicals required :

(a) Cu^{2+} and Fe^{3+} mixture: 24 g ferric alum, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (F.W. = 964.3) and 12.5 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (F.W. = 249.5) dissolve first in a mixture of 100 ml distilled water and 10 ml C. H_2SO_4 which finally dilute to 1000 ml.

(b) Standard (N/20) $\text{K}_2\text{Cr}_2\text{O}_7$ solution

(c) \sim (N/20) sodium thiosulphate solution

(d) 10% KI solution

(e) 1% Starch solution

(f) BDS indicator

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(g) 1:1 aqueous NH_3

(h) 6(N) and 9(N) HCl, (i) Al-foil, (j) Syrupy H_3PO_4

Procedure :

(a) **Estimation of Cu^{2+}** : Same as discussed earlier for estimation of Cu^{2+} in CuSO_4 .

(b) **Estimation of Fe^{3+}** : Pipette out again 25 ml the supplied solution into a 500 ml beaker, diluted with 50 ml distilled water and added 1:1 aqueous NH_3 solution drop wise with stirring until a permanent strong smell of NH_3 appears. The mixture is digested without boiling on a low flame for 5 minutes. It is then cooled and filtered through Whatman No. 41 filter paper. The beaker and the precipitate is washed thoroughly by 20 ml 0.1% NH_4Cl solution containing little NH_3 taking 5 ml each time through spraying with the help of a fine narrow jet mouth dropper. The original beaker is placed under the funnel, dissolved the $\text{Fe}(\text{OH})_3$ in minimum volume of hot 6(N) HCl and washed the filter paper with 100 ml of hot distilled water in portions and collected all the Fe^{3+} solution and the washing together into the beaker. The filter paper is washed with 2 ml 1 : 1 NH_3 drop wise and Fe^{3+} is reprecipitate as $\text{Fe}(\text{OH})_3$ by aqueous NH_3 as usual. $\text{Fe}(\text{OH})_3$ is filtered again through the same filter paper. The precipitate is washed as above to remove Cu^{2+} ion completely. The $\text{Fe}(\text{OH})_3$ is dissolved and the filter paper is washed to free from any yellow stain step by step by using alternatively a total of 50 ml hot 9(N) HCl and 20 ml hot distilled water. All the solutions are collected into the same original beaker. The solution is heated near to boiling and Fe^{3+} is reduced to Fe^{2+} completely by introducing few pieces of Al-foils step by step with constant stirring until the formation of a clear solution through boiling. 100 ml distilled water is added immediately and cooled the beaker to room temperature rapidly under the tap water. 5 ml H_3PO_4 , 4-6 drops of BDS indicator are added and the solution is titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution as usual.

Experimental data : Titration tables are same as earlier

Calculations :

(a) **For Cu^{2+} estimation** : Same as discussed earlier for estimation of Cu^{2+} in CuSO_4 .

(b) **For Fe^{3+} estimation** : As discussed earlier for estimation of Fe^{3+} in ferric salt

Complexometric titration

5.1. General discussion :

The volumetric estimation of metal ions through the formation of complex with a strong multidentate chelating ligand using suitable metal indicator is called complexometric titration or complexometry. A polydentate ligand is able to form a very stable complex with a metal ion which is called chelate and the ligand is called chelating ligand. So, the titration in that sense is called chelatometric titration.

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For a feasible complexometric titration the following conditions should be fulfilled:

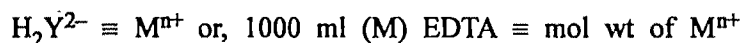
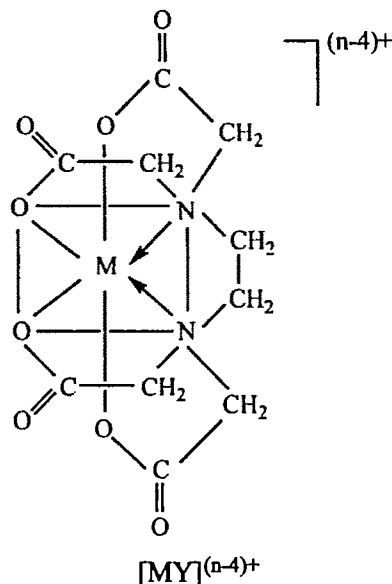
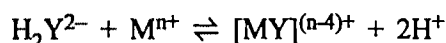
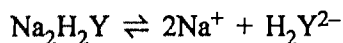
(i) The coordination number of the metal ion must be satisfied completely by the chelating ligand to form a stable water soluble complex.

(ii) The value of stability constant of the complex should be high enough.

(iii) The rate of complex formation reaction should be fast.

(iv) Suitable indicator must be available to detect the sharp end point of the titration.

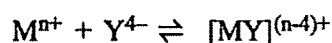
Ethylene diaminetetraacetic acid (EDTA) is available in form of its water soluble disodium salt, $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (Mol. Wt. = 372.24) which is a hexadentate chelating ligand and is able to form (1:1) stable complex with many metal ions satisfying all the above conditions. Hence, it is widely used in complexometric titrations. It ionizes in water as H_2Y^{2-} to form (1:1) stable chelates with many metal ions (M^{n+}) with simultaneously release of H^+ ions as:



The reaction is pH sensitive. Optimum pH values of some metal ions in EDTA titrations are:

M^{n+}	Ca^{2+}	Mg^{2+}	Zn^{2+}	Fe^{3+}	Al^{3+}	Cu^{2+}
pH	10–12	10–12	9–10	12	5–8	5–10

In general, chelate formation reactions are as:



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So, the stability constant (K) of a chelate in its formation reaction is expressed as:

$$K = \frac{[MY]^{(n-4)+}}{[M^{n+}] [Y^{4-}]}$$

Stability constant (K) of some metal complexes are as :

Metal ion	log K
Mg ²⁺	8.7
Ca ²⁺	10.7
Mn ²⁺	13.8
Fe ²⁺	14.3
Co ²⁺	16.3
Zn ²⁺	16.7
Ni ²⁺	18.6
Cu ²⁺	18.8
Fe ³⁺	25.3

Titration curves :

In estimation of Mⁿ⁺ ions by EDTA, if pM (i.e., $-\log[M^{n+}]$) is plotted against the volume of EDTA solution added at the different stages of the titration, then the shape of the curves that would be obtained for different metal ions are in general shown in the figure:

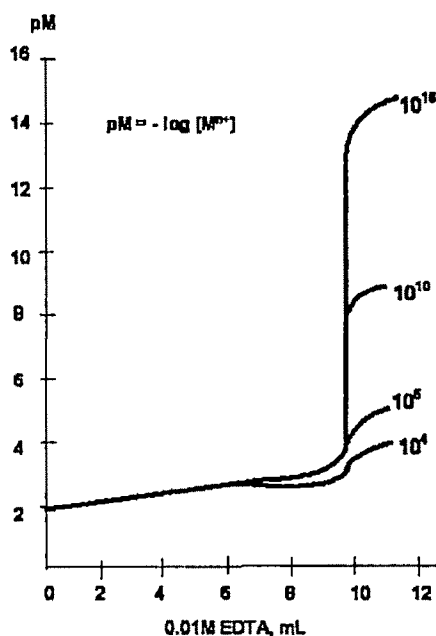


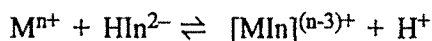
Fig: 5.1 : Titration of 10 ml 0.01 (M) Mⁿ⁺ ion solution vs. 0.01 (M) EDTA solution (of different metal ions)

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The stability constants (K) of the different metal-EDTA complexes are indicated at the right hand side of the curves. The equivalence point is specified by the central point (E) of the flexion region of the curves. It is evident that the greater the value of stability constant (K), the steeper is the flexion region showing sharper end point of the titration. The curves are highly comparable to the acid-base titration curves (pH vs. volume of acid/base). Metal ion sensitive indicator called metal indicator is practically used to detect the end point of the titration. Such indicators are typical organic dyes which are able to form chelates with metal ions reversibly and are able to show sudden colour change at the equivalence point.

Metal Indicators

Metal indicators are normally organic weak acidic dyes and form coloured metal-indicator chelates at the pH, where the metal-EDTA chelates are formed optimally. The metal-indicator chelate is intensely coloured and is different from that of the colour of the free indicator. The stability constant of metal-indicator complex is always lower than the metal-EDTA complex, for which EDTA is able to displace the indicator from metal-indicator complex completely towards the end point and thus colour change occurs.

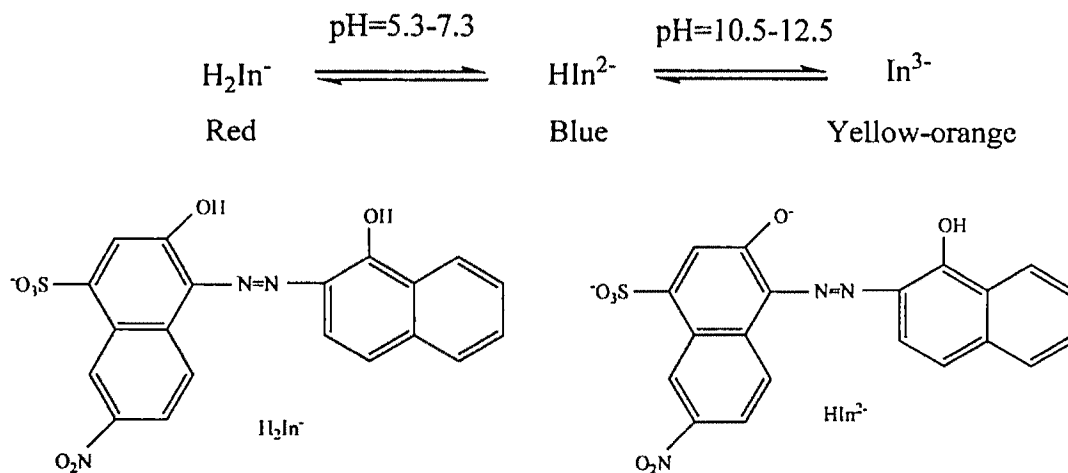


Metal-indicator complex (intense colour)

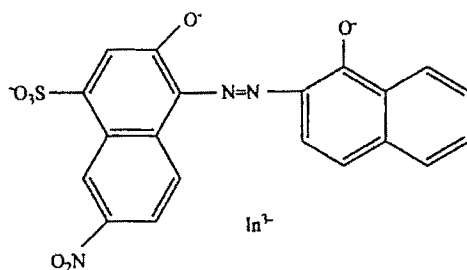


Free indicator colour

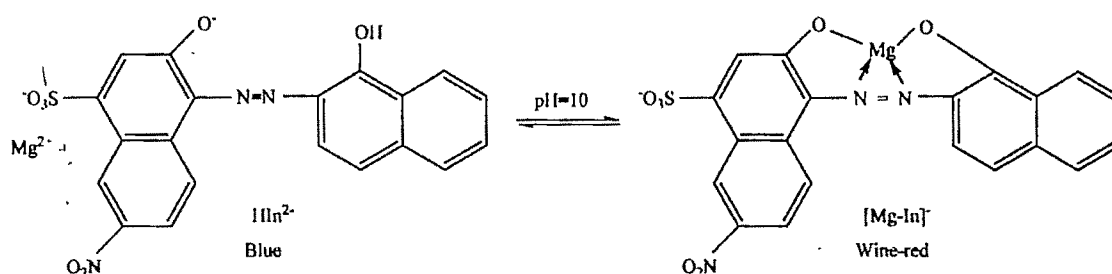
Most commonly used metal indicator is Eriochrome Black T (EBT) (other name Solochrome Black T). EBT (H_2In^-) in solution exhibits the following acid-base behavior.



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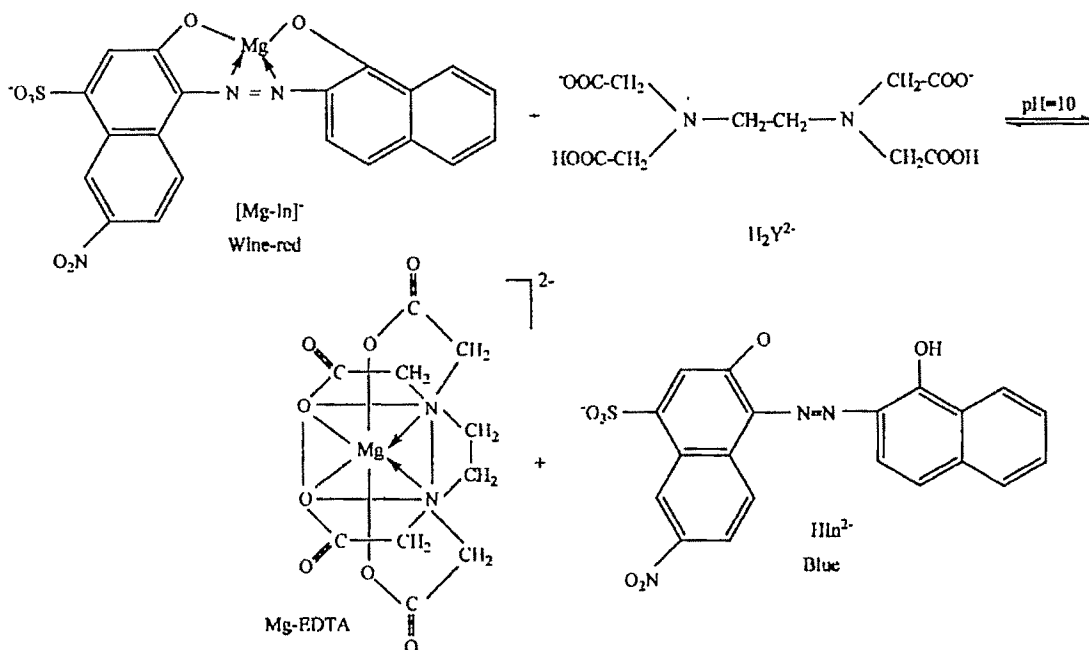


Step 1:



Step 2 :

In 7-10 pH ($\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ buffer), Ca^{2+} , Mg^{2+} , Zn^{2+} etc. show colour change from blue to wine-red releasing an H^+ .



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Choice of metal ion indicators in complexometric titration :

A good metal ion indicator should possess the following characteristics :

- (i) Metal-indicator complex must possess sufficient stability but the stability must be less than that of metal-EDTA complex.
- (ii) Before the end point, when almost all the metal ions are complexes with EDTA the solution should be intensely coloured.
- (iii) The colour reaction must be specific or at least selective.
- (iv) There must be sharp contract in colour between the free indicator and metal-indicator complex.
- (v) The indicator must be very sensitive to the metal ions.
- (vi) The indicator should fulfill these requirements within pH range at which the titration is done.

Some of the commonly used metal indicators are :

Sl	Indicator	Colour		Metal ions (pH range)
		M-In complex	Free In	
1.	EBT	Wine-red	Blue	Ca^{2+} , Mg^{2+} , Zn^{2+} (7-10)
2.	Patton-Reeder's	Red	Blue	Ca^{2+} (12-14)
3.	Murexide	Red-Yellow	Blue-violet	Ca^{2+} (12)
4.	Calcon	Pink	Blue	Ca^{2+} (12)

Type of titrations :

1. Direct titration :

When suitable metal indicators are available and the reaction of EDTA with metal ions are fast, then direct titration of metal ions with EDTA can be done. Examples : Mg^{2+} , Ca^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} .

2. Back titration :

For a slow reaction of EDTA with metal ions or no suitable metal-indicators are available in such case back titration is suitable. Example: Cr^{3+} , Al^{3+} etc.

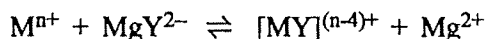
A measured excess of EDTA is then boiled with metal ions maintaining proper condition and then the excess EDTA is back titrated with standard zinc acetate solution using EBT or other indicators.

3. Substitution reaction :

When the metal ions do not react with the indicator or the metal ions form more stable

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complex with EDTA than other metals like Mg^{2+} , Ni^{2+} etc., then substitution method may be applied. In that case, Mg-EDTA complex is treated with the metal ions and then the equivalent amount of displaced Mg^{2+} is titrated with standard EDTA using EBT indicator.



4. Indirect titration :

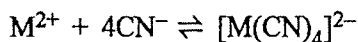
PO_4^{3-} or SO_4^{2-} for example, is precipitated quantitatively first as their respective insoluble compound like MgNH_4PO_4 or BaSO_4 which is then dissolved and treated with measured excess EDTA. Then by back titrating the excess EDTA with standard zinc acetate using EBT indicator, PO_4^{3-} or SO_4^{2-} may be estimated.

5. Selectivity of EDTA titration :

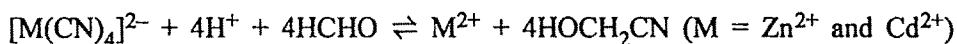
EDTA is a very potential chelating agent to di-, tri-, tetra- valent cations and is thus an unselective reagent. The following methods may, however, be adopted in favour of its selective functioning.

(i) **By controlling the pH of the reaction medium :** The method is based upon the fact that the stability of the M-EDTA complexes are different at different pH of the reaction medium. For example, Bi^{3+} and Pb^{2+} can be titrated in a mixture with success by titrating first Bi^{3+} ions at $\text{pH} = 2$ by EDTA using Xylenol orange as indicator, then adding hexamine to raise pH at 5 and titrating the Pb^{2+} .

(ii) **By the use of masking and demasking reagents :** Masking is defined as a process in which a reacting component (without physical separation of it or its reaction products) is so transformed (by the auxiliary agent) that it does not enter into a particular reaction. Demasking is a process in which the masked substance regains its ability to enter into a particular reaction. For example, the masking agent CN^- forms stable complexes with Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ , Hg^{2+} etc. but not with Mn^{2+} , Pb^{2+} and alkaline earths Ca^{2+} , Mg^{2+} , etc.



Hence, metal ions like Mn^{2+} , Pb^{2+} , Ca^{2+} , Mg^{2+} , etc. can be estimated in presence of Co^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} , etc. ions by the use of excess NaCN/KCN. The cyanide complexes can be demasked by the use of formaldehyde-acetic acid solution or by chloral hydrate or by other specific reagents.



The use of masking and selective demasking agents helps the successive titration of many metal ions. For example, a solution containing Cu^{2+} , Zn^{2+} and Mg^{2+} can be titrated as follows:

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- (i) A given volume of the mixture is titrated with standard EDTA solution using EBT as indicator which corresponds to the total amount of all the metals are present.
- (ii) Adding excess of KCN solution to the same volume of the mixture and following the same titration as before gives only the amount of Mg^{2+} present.
- (iii) Adding excess formaldehyde-acetic acid (demasking agent) in 3 : 1 ratio to the above titrated solution (ii) to liberate Zn^{2+} from the cyanide complex, and titrating the resulting solution till the indicator turns blue gives only the amount of Zn^{2+} present. The Cu^{2+} content may then be found by difference.

5.2. Specification :

A. Preparation of EDTA solution :

EDTA is available commercially in the form of water soluble crystalline disodium salt, $Na_2H_2EDTA \cdot 2H_2O$. (F.W. = 372.24). It absorbs moisture and therefore can not be used as a primary standard. To prepare a 250 ml (M/50) solution nearly 1.87 g EDTA is weighted out, dissolved in ion-free water uniformly by shaking and stored in a polythene bottle. As it is a secondary standard solution, it needs standardization each time before or after use.

B. Preparation of Zinc acetate solution :

Zinc acetate is available as $Zn(OAc)_2 \cdot 2H_2O$ (F.W. = 219.38) and is used as the primary standard for standardization of EDTA solution. Due to hydrolysis the salt solution becomes hazy. To prevent this, it is dissolved in 2% NH_4Cl solution. For the preparation of 250 ml standard (M/50) zinc acetate solution, at first nearly 5 g NH_4Cl is taken into the volumetric flask, then weighted out accurately (nearly 1g, say W g) the amount of Zinc acetate into the same flask and mixed uniformly with ion-free water upto the mark of the volumetric flask. Strength factor of Zinc acetate solution = wt. taken / wt. to be taken = $W/1.0969$ (M/50)

C. Preparation of EBT indicator :

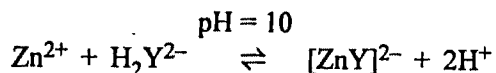
About 0.05 g dyestaff and 5.0 g $KNO_3/NaCl/KCl$ (A.R. grade) are grinded in a glass mortar and the fine solid mixture (1% EBT) is stored in an air-tight plastic container. Alternatively 0.4% methanolic solution of EBT may be used for a month.

D. Standardization of EDTA solution :

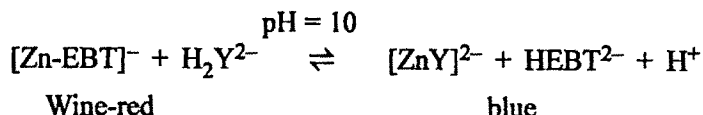
Theory :

EDTA solution may be standardized against standard Zn-acetate solution in presence of NH_4Cl-NH_4OH buffer (pH=10) using EBT as indicator. The end point is identified by the sharp colour change from wine-red to blue.

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Firstly Zn^{2+} forms a stable Zn-EDTA complex with EDTA. Then EDTA displaces free blue EBT indicator from the less stable wine-red coloured Zn-EBT complex forming more stable Zn-EDTA complex at the equivalence point.



Chemicals required:

- 250 ml standard Zinc acetate solution (M/50) is prepared as discussed earlier.
- NH_4Cl - NH_4OH buffer (pH=10): 18 g NH_4Cl (A.R.), 150 ml conc. NH_3 (sp. Gr. 0.90) and 100 ml ion free water are mixed carefully to obtain 250 ml buffer (pH=10) solution.
- EBT indicator (1%) as described earlier.
- ~ (M/50) EDTA solution: Preparation as described earlier.

Procedure:

25 ml standard zinc acetate solution is pipetted out into a 250 ml conical flask. Added successively 50 ml ion free water, 5 ml NH_3 - NH_4Cl buffer solution of pH = 10 and a pinch of Eriochrome Black-T (EBT) indicator. Titrated the resulting mixture with the supplied (M/50) EDTA until the colour changes sharply from wine-red to blue. The titration is repeated to get concordant results.

Experimental data :

No. of titrations	Vol. of zinc acetate solution taken (ml)	Burette reading of standard EDTA solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

Calculation :

Let, (i) an accurate weight of $\text{Zn}(\text{OAc})_2$ taken to prepare 250 ml (M/50) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ solution = W g

$$\therefore \text{Strength of } \text{Zn}(\text{OAc})_2 \text{ solution} = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{1.0969 \left(\frac{M}{50} \right)} = \frac{W}{54.845} (M) = f(M)$$

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(ii) For 25 ml f (M) zinc acetate solution, volume of EDTA required in titration is = V_{st} ml

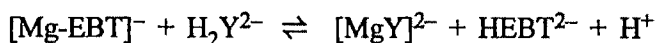
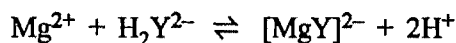
$$\therefore \text{Strength of EDTA} = \frac{25 \times f}{V_{st}}(M) = \frac{25}{V_{st}} \times \frac{W}{54.845}(M) = 0.45583 \times \frac{W}{V_{st}}(M) = S(M)$$

E. Use of standard EDTA solution :

(i) Estimation of Magnesium in Magnesium salt solution :

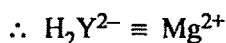
Theory :

Mg^{2+} readily reacts with EDTA to form a stable Mg-EDTA complex and also reacts with EBT to form a less stable wine-red Mg-EBT indicator complex in the pH range 7 to 10. In course of titration EDTA first reacts with free Mg^{2+} ion to form Mg-EDTA complex and then reacts with wine-red coloured Mg-EBT complex to displace free blue coloured EBT indicator of the solution at the end point.



Wine-red

blue



or, 1000 ml (M) EDTA solution \equiv 24.32 g of Mg^{2+}

Chemicals required :

- (a) For (M/50) Mg^{2+} solution: 5 g $MgSO_4 \cdot 7H_2O$ is dissolved in 1000 ml 0.1(N) H_2SO_4 .
- (b) 250 ml standard Zinc acetate solution (M/50) is prepared as discussed earlier.
- (c) NH_4Cl-NH_4OH buffer (pH=10) : 18 g NH_4Cl (A.R.), 150 ml conc. NH_3 (Sp. Gr. 0.90) and 100 ml ion free water are mixed carefully to obtain 250 ml buffer (pH = 10) solution.
- (d) EBT indicator (1%) as described earlier.
- (e) \sim (M/50) EDTA solution

Procedure :

25 ml of supplied Mg^{2+} solution is pipette out into a 250 ml conical flask and it is made slightly ammoniacal by dropwise addition of (1:1) NH_4OH solution with shaking. 50 ml ion-free water, 5 ml NH_4OH-NH_4Cl buffer solution (pH = 10) and a pinch of Eriochrome Black-T (EBT) indicator are added. The resulting solution is titrated with standardized (M/50) EDTA solution until the colour changes sharply from wine-red to blue. The titration is repeated to get concordant results.

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Experimental data :

(a) Table for standardization: As earlier

(b) Table for estimation of Mg^{2+} :

No. of titrations	Vol. of Mg^{2+} salt solution taken (ml)	Burette reading of standard EDTA solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

Calculation :

Let,

(i) an accurate weight of $Zn(OAc)_2$ taken to prepare 250 ml (M/50) $Zn(OAc)_2 \cdot 2H_2O$ solution = W g

$$\therefore \text{Strength of } Zn(OAc)_2 \text{ solution} = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{1.0969 \left(\frac{M}{50} \right)} = \frac{W}{54.845} (M) = f(M)$$

(ii) For 25 ml f(M) zinc acetate solution, volume of EDTA required in titration = V_{st} ml

$$\therefore \text{Strength of EDTA} = \frac{25 \times f}{V_{st}} (M) = \frac{25}{V_{st}} \times \frac{W}{54.845} (M) = 0.45583 \times \frac{W}{V_{st}} (M) = S(M)$$

(iii) For 25 ml supplied Mg^{2+} salt solution, the volume of EDTA in titration required is = V_{Mg} ml.

$$1000 \text{ ml (M) EDTA} = 24.32 \text{ g } Mg^{2+}$$

$$\therefore V_{Mg} \text{ ml } S(M) \text{ EDTA} = 0.02432 \times V_{Mg} \times S \text{ g } Mg^{2+}$$

$$25 \text{ ml } Mg^{2+} \text{ salt solution contains} = 0.02432 \times V_{Mg} \times S \text{ g } Mg^{2+}$$

$$\therefore 1000 \text{ ml } Mg^{2+} \text{ salt solution contains} = 0.02432 \times 40 \times V_{Mg} \times S \text{ g } Mg^{2+}$$

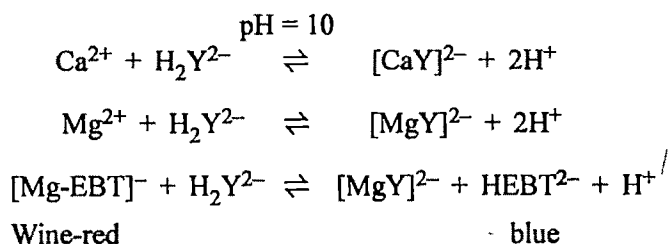
$$= 0.02432 \times 40 \times V_{Mg} \times 0.45583 \times \frac{W}{V_{st}} \text{ g } Mg^{2+}$$

$$= 0.44343 \times W \times \frac{V_{Mg}}{V_{st}} \text{ g } Mg^{2+}$$

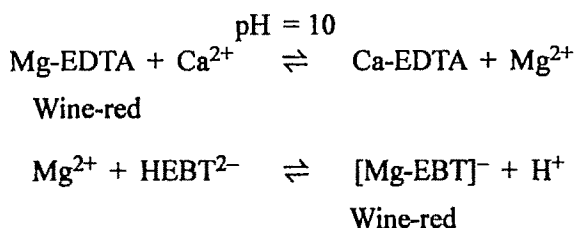
$$\therefore \text{Therefore, } Mg^{2+} \text{ present in supplied magnesium salt solution} = 0.44343 \times W \times \frac{V_{Mg}}{V_{st}} \text{ g/L}$$

(ii) Estimation of Calcium in Calcium salt solution :**Theory :**

Ca^{2+} readily reacts with EDTA to form a relatively stable Ca-EDTA complex. It also reacts with EBT to form a very unstable Ca-EBT complex so that no sharp end point is obtained. Mg-EBT complex is more stable than Ca-EBT complex but less stable than Mg-EDTA complex. The order of stability of the complexes are: Ca-EDTA > Mg-EDTA > Mg-EBT > Ca-EBT.



As a result to get a sharp end point from wine-red to blue a small amount of Mg^{2+} ion must be present in the solution of Ca^{2+} . This is done by adding a small amount of Mg-EDTA complex to the solution of Ca^{2+} before starting the titration.



\therefore 1000 ml (M) EDTA solution \equiv 40.08 g Ca^{2+}

Chemicals required :

(a) For (M/50) Ca^{2+} solution: 2 g CaCO_3 is dissolved in minimum quantity 6(N) HCl and then diluted to one litre. (b) 250 ml standard Zinc acetate solution (M/50) is prepared, as discussed earlier. (c) $\text{NH}_4\text{Cl-NH}_4\text{OH}$ buffer (pH=10), as described earlier. (d) EBT indicator (1%), as described earlier. (e) 0.1 (M) Mg-EDTA solution. (f) \sim (M/50) EDTA solution.

Procedure :

25 ml of supplied Ca^{2+} solution is pipette out into a 250 ml conical flask and it is made ammoniacal by drop wise adding of (1:1) NH_4OH with shaking the flask. Added successively 50 ml ion-free water, 5 ml $\text{NH}_4\text{Cl-NH}_4\text{OH}$ buffer (pH = 10), 5 drops of 0.1 (M) Mg-EDTA complex solution and a pinch of Eriochrome Black-T (EBT) indicator. The resultant mixture

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is then titrated with standardized (M/50) EDTA solution until the colour changes sharply from wine-red to blue.

Experimental data : Table: Similar as before.

Calculation :

Let,

- (i) an accurate weight of $\text{Zn}(\text{OAc})_2$ taken to prepare 250 ml (M/50) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ solution = W g

$$\therefore \text{Strength of } \text{Zn}(\text{OAc})_2 \text{ solution} = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{1.0969} \left(\frac{M}{50} \right) = \frac{W}{54.845} (M) = f(M)$$

- (ii) For 25 ml f (M) zinc acetate solution, volume of EDTA required in titration = V_{st} ml

$$\therefore \text{Strength of EDTA} = \frac{25 \times f(M)}{V_{st}} = \frac{25}{V_{st}} \times \frac{W}{54.845} (M) = 0.45583 \times \frac{W}{V_{st}} (M) = S(M)$$

- (iii) For 25 ml supplied Ca^{2+} salt solution, the volume of EDTA in titration required = V_{Ca} ml.

$$1000 \text{ ml } (M) \text{ EDTA} = 40.08 \text{ g } \text{Ca}^{2+}$$

$$\therefore V_{Ca} \text{ ml } S(M) \text{ EDTA} = 0.04008 \times V_{Ca} \times S \text{ g } \text{Ca}^{2+}$$

$$25 \text{ ml } \text{Ca}^{2+} \text{ salt solution contains} = 0.04008 \times V_{Ca} \times S \text{ g } \text{Ca}^{2+}$$

$$\therefore 1000 \text{ ml } \text{Ca}^{2+} \text{ salt solution contains} = 0.04008 \times 40 \times V_{Ca} \times S \text{ g } \text{Ca}^{2+}$$

$$= 0.04008 \times 40 \times V_{Ca} \times 0.45583 \times \frac{W}{V_{st}} \text{ g } \text{Ca}^{2+}$$

$$= 0.7307866 \times W \times \frac{V_{Ca}}{V_{st}} \text{ g } \text{Ca}^{2+}$$

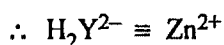
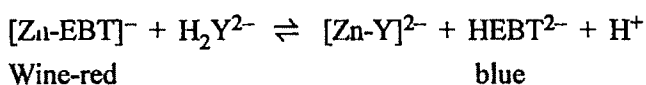
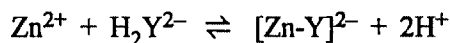
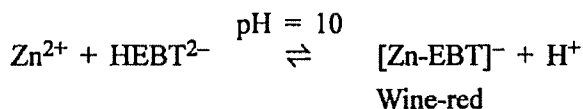
$$\therefore \text{Therefore, } \text{Ca}^{2+} \text{ present in supplied calcium salt solution} = 0.7307866 \times W \times \frac{V_{Ca}}{V_{st}} \text{ g/L}$$

(iii) Estimation of Zinc in Zinc salt solution :

Theory :

Zn^{2+} can be estimated with EDTA at pH 10 using EBT as indicator. At first Zn^{2+} reacts with EBT to form a stable wine-red coloured Zn-EBT complex. Then Zn^{2+} reacts with EDTA to form Zn-EDTA complex. But as the stability of Zn-EDTA is greater than Zn-EBT complex, EDTA displaces free blue coloured EBT indicator from Zn-EBT to form more stable Zn-EDTA complex. Consequently the change of colour from wine-red to blue that marks the equivalence point.

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or, 1000 ml (M) EDTA solution \equiv 65.4 g Zn^{2+}

Chemicals required :

- (a) 5.8 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (F.W. = 287.4) is dissolved in slight H_2SO_4 (3ml conc. $\text{H}_2\text{SO}_4/\text{lit}$) containing one litre water.
- (b) 250 ml standard Zinc acetate solution (M/50) is prepared as discussed earlier.
- (c) $\text{NH}_4\text{Cl-NH}_4\text{OH}$ buffer (pH = 10), as described earlier. (d) EBT indicator (1%) as described earlier.
- (e) \sim (M/50) EDTA solution

Procedure :

25 ml standard Zn^{2+} solution is pipetted out into a 250 ml conical flask and it is made ammoniacal by drop wise adding of (1 : 1) NH_4OH with shaking the flask. Added successively 50 ml ion free water, 5 ml $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution of pH = 10 and a pinch of Eriochrome Black-T (EBT) indicator. The resulting mixture is titrated with the supplied (M/50) EDTA until the colour changes sharply from wine-red to blue. The titration is repeated to get concordant results.

Experimental data : Table same as earlier.

Calculation :

- (i) An accurate weight of $\text{Zn}(\text{OAc})_2$ taken to prepare 250 ml (M/50) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ solution = W g

$$\therefore \text{Strength of } \text{Zn}(\text{OAc})_2 \text{ solution} = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{1.0969 \left(\frac{M}{50} \right)} = \frac{W}{54.845} (M) = f(M)$$

- (ii) For 25 ml f(M) zinc acetate solution, volume of EDTA required in titration is = V_{st} ml

$$\therefore \text{Strength of EDTA} = \frac{25 \times f(M)}{V_{st}} = \frac{25}{V_{st}} \times \frac{W}{54.845} (M) = 0.45583 \times \frac{W}{V_{st}} (M) = S(M)$$

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(iii) For 25 ml supplied Zn^{2+} salt solution, the volume of EDTA in titration required = V_{Zn} ml.

$$1000 \text{ ml (M) EDTA} = 65.4 \text{ g Zn}^{2+}$$

$$\therefore V_{\text{Zn}} \text{ ml S(M) EDTA} = 0.0654 \times V_{\text{Zn}} \times S \text{ g Zn}^{2+}$$

$$25 \text{ ml Zn}^{2+} \text{ salt solution contains} = 0.0654 \times V_{\text{Zn}} \times S \text{ g Zn}^{2+}$$

$$\therefore 1000 \text{ ml Zn}^{2+} \text{ salt solution contains} = 0.0654 \times 40 \times V_{\text{Zn}} \times S \text{ g Zn}^{2+}$$

$$= 0.0654 \times 40 \times V_{\text{Zn}} \times 0.45583 \times \frac{W}{V_{\text{st}}} \text{ g Zn}^{2+}$$

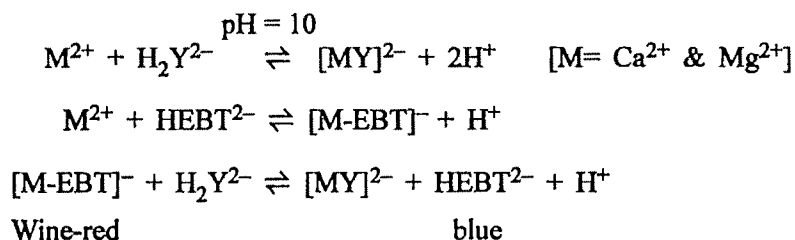
$$= 1.19245 \times W \times \frac{V_{\text{Zn}}}{V_{\text{st}}} \text{ g Zn}^{2+}$$

$$\therefore \text{Therefore, Zn}^{2+} \text{ present in supplied zinc salt solution} = 1.19245 \times W \times \frac{V_{\text{Zn}}}{V_{\text{st}}} \text{ g/L}$$

(iv) Estimation of Calcium and Magnesium in a Mixture:

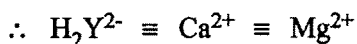
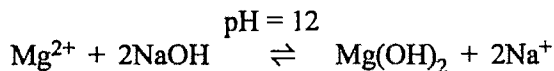
Theory :

Both Ca^{2+} and Mg^{2+} form stable complexes with EDTA at pH = 10 ($\text{NH}_4\text{Cl-NH}_4\text{OH}$ buffer). The total (Ca^{2+} and Mg^{2+}) content in a measured volume of the mixture can be estimated by titrating with standard EDTA solution using EBT as indicator. Both Ca^{2+} and Mg^{2+} react with EDTA and also with EBT to produce their respective complexes having different stability. Stability order: $\text{Ca-EDTA} > \text{Mg-EDTA} > \text{Mg-EBT} > \text{Ca-EBT}$. As the titration proceeds, EDTA first reacts with free Ca^{2+} and Mg^{2+} to form the stable metal-EDTA complexes. After complete reaction with metal ions, EDTA displaces free blue coloured EBT indicator from wine-red M-EBT complexes at the equivalence point. Consequently, the change of colour from wine-red to blue that marks the equivalence point. The volume of EDTA consumed corresponds to the total amount of Ca^{2+} and Mg^{2+} present into the measured volume of the mixture.



Treatment of the same volume of the mixture with NaOH solution ($\text{pH} \geq 12$), $\text{Mg}(\text{OH})_2$ is precipitated quantitatively. Ca^{2+} present in the solution alone can be estimated by titrating with standard EDTA solution using calcon or Patton-Reeders indicator. The volume of EDTA here corresponds only to the amount of Ca^{2+} present. Difference between the two titre values corresponds to the amount of Mg^{2+} present in the supplied solution.

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or, 1000 ml of (M) EDTA solution \equiv 40.08 g $\text{Ca}^{2+} \equiv$ 24.32 g Mg^{2+}

Chemicals required :

- (a) To prepare Ca^{2+} and Mg^{2+} solution, 1 g CaCO_3 and 1 g MgCO_3 mixture is dissolved in minimum quantity of 6(N) HCl and diluted to one litre.
- (b) Patton-Reeder's indicator : 1% in NaCl/KCl/ KNO_3 . Preparation method is same as EBT.
- (c) 10% NaOH solution: 10 g NaOH is dissolved in 100 ml ion-free water.
- (d) 250 ml standard Zn-acetate solution (M/50) is prepared as discussed earlier.
- (e) \sim (M/50) EDTA solution

Procedure

- (a) **For Ca^{2+} and Mg^{2+} :** 25 ml aliquot of the given (Ca^{2+} & Mg^{2+}) mixed solution is pipetted out into a 250 ml conical flask and is neutralized with 1:1 aqueous NH_3 , until a faint smell of NH_3 appears. 25 ml distilled/ion-free water, 5 ml NH_4Cl - NH_4OH buffer (pH = 10) and a pinch of Erichrome Black-T (EBT) indicator are added. The resulting solution is titrated with standard EDTA solution until the colour change from wine-red to blue. The titration is repeated to get concordant results.
- (b) **For Ca^{2+} :** 25 ml aliquot of the given mixture is again pipetted out into a 250 ml conical flask and is neutralized with 1:1 NH_3 as above. 25 ml ion-free water, 10 ml of 10% fresh NaOH solution, a pinch of Patton-Reeder's indicator are added and mixed well by shaking. The resulting solution is titrated with standard EDTA solution until the colour changes from wine-red to blue. The titration is repeated to get concordant results.

Experimental data :

(a) Table for standardization : As earlier

(b) Table for estimation of Ca^{2+} and Mg^{2+} :

No. of titrations	Vol. of stock solution taken (ml)	Burette reading of standard EDTA solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

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(c) Table for estimation of Ca^{2+} :

No. of titrations	Vol. of stock solution taken (ml)	Burette reading of standard EDTA solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

Calculation:

Let us consider the following:

- (i) An accurate weight of $\text{Zn}(\text{OAc})_2$ is taken to prepare 250 ml (M/50) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ solution = W g

$$\therefore \text{Strength of } \text{Zn}(\text{OAc})_2 \text{ solution} = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{1.0969 \left(\frac{M}{50} \right)} = \frac{W}{54.845} (M) = f(M)$$

- (ii) For 25 ml f(M) zinc acetate solution, volume of EDTA required in titration is = V_{st} ml

$$\therefore \text{Strength of EDTA} = \frac{25 \times f(M)}{V_{st}} = \frac{25}{V_{st}} \times \frac{W}{54.845} (M) = 0.45583 \times \frac{W}{V_{st}} (M) = S(M)$$

- (iii) For 25 ml supplied (Ca^{2+} & Mg^{2+}) solution, the volume of standard EDTA in titration required = V_T ml.

- (iv) For 25 ml supplied Ca^{2+} solution [where Mg^{2+} precipitated as $\text{Mg}(\text{OH})_2$], the volume of standard EDTA in titration required = V_{Ca} ml.

For Ca^{2+} :

$$1000 \text{ ml (M) EDTA} = 40.08 \text{ g } \text{Ca}^{2+}$$

$$\therefore V_{Ca} \text{ ml } S(M) \text{ EDTA} = 0.04008 \times V_{Ca} \times S \text{ g } \text{Ca}^{2+}$$

$$25 \text{ ml } \text{Ca}^{2+} \text{ salt solution contains} = 0.04008 \times V_{Ca} \times S \text{ g } \text{Ca}^{2+}$$

$$\therefore 1000 \text{ ml } \text{Ca}^{2+} \text{ salt solution contains} = 0.04008 \times 40 \times V_{Ca} \times S \text{ g } \text{Ca}^{2+}$$

$$= 0.04008 \times 40 \times V_{Ca} \times 0.45583 \times \frac{W}{V_{st}} \text{ g } \text{Ca}^{2+}$$

$$= 0.730786 \times W \times \frac{V_{Ca}}{V_{st}} \text{ g } \text{Ca}^{2+}$$

$$\therefore \text{Therefore, } \text{Ca}^{2+} \text{ present in supplied mixed salt solution} = 0.730786 \times W \times \frac{V_{Ca}}{V_{st}} \text{ g/L}$$

For Mg^{2+} :

$$1000 \text{ ml (M) EDTA} = 24.32 \text{ g Mg}^{2+}$$

$$\therefore (V_T - V_{Ca}) \text{ ml S(M) EDTA solution} = 0.02432 \times (V_T - V_{Ca}) \times S \text{ g Mg}^{2+}$$

$$25 \text{ ml mixed solution contain} = 0.02432 \times (V_T - V_{Ca}) \times S \text{ g Mg}^{2+}$$

$$\therefore 1000 \text{ ml mixed solution contain} = 0.02432 \times 40 \times (V_T - V_{Ca}) \times S \text{ g Mg}^{2+}$$

$$= 0.02432 \times 40 \times (V_T - V_{Ca}) \times 0.45583 \times \frac{W}{V_{st}} \text{ g Mg}^{2+}$$

$$= 0.443431 \times W \times \frac{V_T - V_{Ca}}{V_{st}} \text{ g Mg}^{2+}$$

$$\therefore \text{Mg}^{2+} \text{ present in mixed supplied solution} = 0.443431 \times W \times \frac{V_T - V_{Ca}}{V_{st}} \text{ g/L}$$

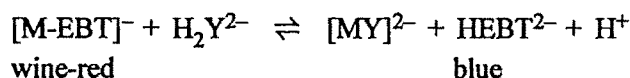
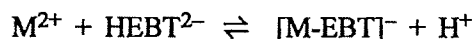
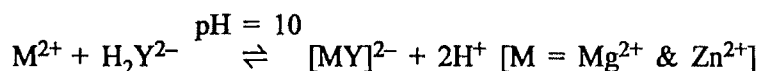
(v) Estimation of Magnesium and Zinc in a Mixture :

Theory :

As both Mg^{2+} and Zn^{2+} form stable complexes with EDTA at pH = 10 ($\text{NH}_4\text{Cl-NH}_4\text{OH}$ buffer), the total (Mg^{2+} and Zn^{2+}) content in a measured volume of the mixture can be estimated by titrating with standard EDTA solution using EBT as indicator.

Mg^{2+} and Zn^{2+} react with EDTA and EBT both to produce their respective complexes having different stability. Stability order: $\text{Zn-EDTA} > \text{Mg-EDTA} > \text{Zn-EBT} > \text{Mg-EBT}$.

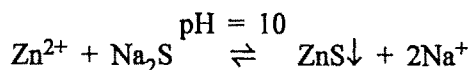
As the titration with EDTA proceeds, Mg^{2+} and Zn^{2+} first react with EDTA to form stable complexes, then EDTA displaces free blue coloured EBT indicator from wine-red M-EBT complexes with the formation of more stable M-EDTA complexes at the equivalence point. Consequently, the change of colour from wine-red to blue marks the equivalence point. The volume of EDTA consumed corresponds to the total amount of Mg^{2+} and Zn^{2+} present into the measured volume of the mixture.



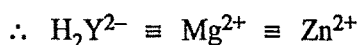
Treatment of the same measured volume of the mixture at pH = 10 ($\text{NH}_4\text{Cl-NH}_4\text{OH}$ buffer) with excess Na_2S solution, ZnS is precipitated quantitatively. Then, Mg^{2+} present in the solution

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alone can be estimated by titrating with standard EDTA solution using EBT as indicator. The volume of EDTA here corresponds only to the amount of Mg^{2+} present.



Difference between the two titre values corresponds to the amount of Zn^{2+} present.



or, 1000 ml of (M) EDTA solution \equiv 24.32 g $\text{Mg}^{2+} \equiv$ 65.4 g Zn^{2+}

Chemicals required :

- For Mg^{2+} and Zn^{2+} solution : 1 g MgCO_3 and 2.5 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (or 1.3 g ZnCO_3) is dissolved in a minimum quantity of dil. HCl to prepare one litre mixed solution.
- 10% Na_2S solution: 10 g Na_2S in 100 ml ion-free water.
- 250 ml standard Zinc acetate solution (M/50) is prepared as discussed earlier.
- NH_4Cl - NH_4OH buffer (pH=10): As discussed earlier.
- EBT indicator (1%) as described earlier.
- ~(M/50) EDTA solution

Procedure :

- For total (Mg^{2+} & Zn^{2+}) : Same as (Ca^{2+} + Mg^{2+}) mixture discussed earlier.
- For Mg^{2+} : 25 ml aliquot of the given mixture is again pipetted out into a 250 ml conical flask and is neutralized with 1 : 1 NH_3 as above. 25 ml ion-free water, 10 ml NH_4Cl - NH_4OH buffer (pH=10), 10 ml 10% freshly prepared Na_2S solution, a pinch of EBT indicator are added and mixed well by shaking. The resulting solution is titrated with standard EDTA solution until the colour changes from dirty wine-red to blue. The titration is repeated to get concordant results.

Experimental data :

(a) Table for standardization : As earlier

(b) Table for estimation of Mg^{2+} and Zn^{2+} :

No. of titrations	Vol. of stock solution taken (ml)	Burette reading of standard EDTA solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

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(c) Table for estimation of Mg^{2+} :

No. of titrations	Vol. of stock solution taken (ml)	Burette reading of standard EDTA solution (ml)			
		Initial	Final	Difference	Most frequent reading
1	25	0			
2	25	0			
3	25	0			

Calculation :

Let,

(i) an accurate weight of $\text{Zn}(\text{OAc})_2$ taken to prepare 250 ml (M/50) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ solution = W g

$$\therefore \text{Strength of } \text{Zn}(\text{OAc})_2 \text{ solution} = \frac{\text{weight taken}}{\text{weight to be taken}} = \frac{W}{1.0969} \left(\frac{M}{50} \right) = \frac{W}{54.845} (M) = f(M)$$

(ii) For 25 ml f(M) zinc acetate solution, volume of EDTA required in titration = V_{st} ml

$$\therefore \text{Strength of EDTA} = \frac{25 \times f(M)}{V_{\text{st}}} = \frac{25}{V_{\text{st}}} \times \frac{W}{54.845} (M) = 0.45583 \times \frac{W}{V_{\text{st}}} (M) = S(M)$$

(iii) For 25 ml supplied total (Mg^{2+} & Zn^{2+}) solution, the volume of standard EDTA in titration required = V_T ml.

(iv) For 25 ml supplied Mg^{2+} solution (where Zn^{2+} precipitated as ZnS), the volume of standard EDTA in titration required = V_{Mg} ml.

For Mg^{2+} :

$$1000 \text{ ml (M) EDTA} = 24.32 \text{ g } \text{Mg}^{2+}$$

$$\therefore V_{\text{Mg}} \text{ ml } S(M) \text{ EDTA} = 0.02432 \times V_{\text{Mg}} \times S \text{ g } \text{Mg}^{2+}$$

$$25 \text{ ml } \text{Mg}^{2+} \text{ salt solution contains} = 0.02432 \times V_{\text{Mg}} \times S \text{ g } \text{Mg}^{2+}$$

$$\therefore 1000 \text{ ml } \text{Mg}^{2+} \text{ salt solution contains} = 0.02432 \times 40 \times V_{\text{Mg}} \times S \text{ g } \text{Mg}^{2+}$$

$$= 0.02432 \times 40 \times V_{\text{Mg}} \times 0.45583 \times \frac{W}{V_{\text{st}}} \text{ g } \text{Mg}^{2+}$$

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$$= 0.443431 \times W \times \frac{V_{Mg}}{V_{st}} \text{ g Mg}^{2+}$$

$$\therefore \text{Mg}^{2+} \text{ present in supplied mixed salt solution} = 0.443431 \times W \times \frac{V_{Mg}}{V_{st}} \text{ g/L}$$

For Zn^{2+} :

$$1000 \text{ ml (M) EDTA} = 65.4 \text{ g Zn}^{2+}$$

$$\therefore (V_T - V_{Mg}) \text{ ml S(M) EDTA solution} = 0.0654 \times (V_T - V_{Mg}) \times S \text{ g Zn}^{2+}$$

$$25 \text{ ml mixed solution contain} = 0.0654 \times (V_T - V_{Mg}) \times S \text{ g Zn}^{2+}$$

$$\therefore 1000 \text{ ml mixed solution contain} = 0.0654 \times 40 \times (V_T - V_{Mg}) \times S \text{ g Zn}^{2+}$$

$$= 0.0654 \times 40 \times (V_T - V_{Mg}) \times 0.45583 \times \frac{W}{V_{st}} \text{ g Zn}^{2+}$$

$$= 1.19245 \times W \times \frac{V_T - V_{Mg}}{V_{st}} \text{ g Zn}^{2+}$$

$$\therefore \text{Zn}^{2+} \text{ present in supplied mixed salt solution} = 1.19245 \times W \times \frac{V_T - V_{Mg}}{V_{st}} \text{ g/L}$$

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Instrumental Analysis

Experiment No. 1 : Spectrophotometric/colorimetric estimation of Mn(II).

A sample containing low manganese content can be conveniently estimated by colorimetric method. The colorimetric determination is based on Lambert-Beer's law, according to which the absorbance (A) of a solution of light absorbing substance is given by

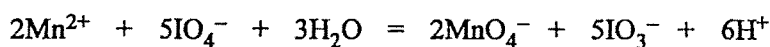
$$A = \epsilon cl,$$

where l is the path length (usually 1 cm), c is the concentration in molarity and ϵ is the molar extinction coefficient. If the absorbance (A) of a series of solutions of known concentrations of the substance to be estimated is plotted against concentration (c), a straight line passing through origin is obtained. The molar extinction coefficient, ϵ , may be obtained from the slope of this straight line. Such a curve is called a calibration curve. The range of concentration of the substance, where the absorbance vs. concentration curve is linear, is the useful range of concentration for colorimetric determination.

Unknown concentration of the substance in a sample solution may be determined by measuring its absorbance for the light of same wave length and then extrapolating the calibration curve or by simply dividing the experimental absorbance by the extinction coefficient.

In colorimetric determinations, optical filters are often used for isolating the desired spectral region from the undesired one. Light filters in the wave length region 500 – 560 nm are generally used in the determination of manganese as MnO_4^- . Alternatively, a spectrophotometer may be used and measurement may be made at 520 nm.

Periodate ion (IO_4^-) quantitatively oxidizes a colorless solution of Mn(II) to pink colored permanganic acid (HMnO_4) in hot dilute nitric or sulfuric acid medium:



The resulting MnO_4^- is estimated colorimetrically/spectrophotometrically. The solution of permanganate ion has two absorption maxima at 520 and 545 nm. By measuring the absorbance of the test solution for either of these wavelengths and comparing the same with the absorbance of a set of standard permanganate solutions, it is possible to determine the concentration of permanganate present in the test sample, since $[\text{MnO}_4^-] \equiv [\text{Mn}^{2+}]$.

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Chemicals and apparatus required :

- a) (~N/20) KMnO_4 solution : Dissolve 0.4–0.5 g of KMnO_4 in distilled water and dilute to 250 ml
- b) (A.R.) KIO_4
- c) 10^{-2} (M) solution of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (F.W. = 169) or $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (F.W. = 223) in 2 (N) H_2SO_4
- d) Standard (N/20) oxalic acid solution: To be prepared by accurate weighing
- e) Colorimeter/Spectrophotometer with matched cells

Procedure :

1. Standardization of KMnO_4 solution:

Take an aliquot of 10 ml of the standard (N/20) oxalic acid in a 100 ml conical flask, add 10 ml 4(N) H_2SO_4 , warm to 60–70°C and titrate with ~ (N/20) KMnO_4 solution until a permanent pink colour persists in the solution. Record the titre value of the KMnO_4 solution and calculate its strength $f(\text{N}/20)$. Dilute 10 ml of this solution to 50 ml in a 100 ml volumetric flask to obtain a standard $f(\text{N}/100)$ KMnO_4 solution, i.e. $f(\text{M}/500)$ KMnO_4 solution.

2. Preparation of standard MnO_4^- solutions:

Take 0.5, 1.0, 2.0, 4.0, 6.0, 8.0 and 10.0 ml of the standard $f(\text{M}/500)$ KMnO_4 solution in separate 25 ml volumetric flasks and dilute each solution upto the mark with 2(N) H_2SO_4 and calculate their concentrations in ppm of manganese.

3. Determination of λ_{max} (or best filter) and verification of Beer's law :

Measure the absorbance of any one of the solutions in the range 600 – 400 nm (or using suitable filters) using 2(N) H_2SO_4 as blank and find λ_{max} or the best filter.

Now measure the absorbance (A) of the remaining standard solutions for the λ_{max} or the best filter. Record the data in a tabular form (Table–1). Use suitably diluted or concentrated solutions to have the absorbance values within 0.1–0.7 range.

Table-1 : Composition of KMnO_4 solutions for verification of Beer's law

λ_{max} (best filter) :nm (No.)

Optical path length : $l = 1$ cm

Total volume of each solution = 25 ml in 2(N) H_2SO_4

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Set	Volume (ml) of (M/500) KMnO_4	$[\text{MnO}_4^-] \times 10^5 (\text{M})$	Mn (ppm)	Absorbance (A)
1.	0.5	4	2.2	
2.	1.0	8	4.4	
3.	1.5	12	6.6	
4.	2.0	16	8.8	
5.	2.5	20	11	
6.	3.0	24	13.2	
7.	3.5	28	15.4	
8.	4.0	32	17.6	
9.	V'	Unknown	Unknown	

4. Preparation of the test solution:

Pipette out 10 ml of the prepared $\sim 10^{-2}$ (M) solution of the Mn(II) salt into a 100 ml volumetric flask, dilute to the mark with 2(N) H_2SO_4 and mix uniformly to obtain $\sim 10^{-3}$ (M) solution of the salt. Take an aliquot of 5 ml from this diluted solution into a 50 ml beaker, add ~ 4.5 ml of 9(N) H_2SO_4 , dilute with ~ 10 ml of distilled water so that acidity of the resulting solution becomes ~ 2 (N). Add 0.2 – 0.3 g of (A.R) KIO_4 and heat gently at 90°C (use a thermometer) on an asbestos board (don't boil) for ~ 5 minutes. Cool to room temperature. Transfer the resulting pink coloured solution quantitatively into a 25 ml volumetric flask, dilute to the mark with distilled water and mix uniformly.

5. Measurement of absorbance of the sample solution :

Measure the absorbance of the sample permanganate solution itself or of a suitably diluted solution prepared by exactly diluting an appropriate volume (V') of this sample solution to 25 ml with 2(N) H_2SO_4 so that the absorbance value falls within the range of concentration in which Beer's law is obeyed.

Calculation:

- (i) Plot the absorbance (A) values of the standard KMnO_4 solutions (sets 1–8) against molar concentrations of permanganate (in $\text{M} \times 10^5$ scale) or manganese in ppm scale. Draw the best straight line passing through the origin and the experimental points as required by Beer's law. Determine the slope of the straight line and calculate ϵ ($\text{lit.mol}^{-1}.\text{cm}^{-1}$)
- (ii) Now match the absorbance (A') of the unknown permanganate solution with the absorbance–concentration plot of the standard permanganate solutions and find the concentration of the unknown permanganate solution graphically.

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- (iii) Alternatively, calculate the concentration of the unknown permanganate solution $[\text{MnO}_4^-]_{\text{uk}}$ using the relation: $[\text{MnO}_4^-]_{\text{uk}} = A' / (\epsilon l) \text{ (M)}$
- (iv) Calculate the amount of the Mn(II) salt, $\text{MnSO}_4 \cdot x\text{H}_2\text{O}$ ($x = 1, 4$) in mg/100ml of the prepared solution.

Strength of the unknown permanganate solution = $[\text{MnO}_4^-]_{\text{uk}} \text{ (M)}$

Now, $[\text{MnO}_4^-] \equiv [\text{Mn}^{2+}] \equiv \text{MnSO}_4 \cdot x\text{H}_2\text{O}$ ($x = 1$, F.W. = 169; $x = 4$, F.W. 223)

Therefore, strength of the original unknown Mn(II) salt solution =

$$\frac{25 \times [\text{MnO}_4^-]_{\text{uk}}}{V'} \times \frac{25}{5} \times \frac{100}{10} \text{ (M)} = 1250 \frac{[\text{MnO}_4^-]_{\text{uk}}}{V'} \text{ (M)}$$

Now, 100 ml 1 (M) $[\text{MnO}_4^-] \equiv 16900 \text{ mg of MnSO}_4 \cdot \text{H}_2\text{O} \equiv 22300 \text{ mg of MnSO}_4 \cdot 4\text{H}_2\text{O}$

Therefore, 100 ml of test solution $\equiv \frac{[\text{MnO}_4^-]_{\text{uk}}}{V'} \times 211.29 \times 10^5 \text{ mg of MnSO}_4 \cdot \text{H}_2\text{O}$

$$\equiv \frac{[\text{MnO}_4^-]_{\text{uk}}}{V'} \times 278.86 \times 10^5 \text{ mg of MnSO}_4 \cdot 4\text{H}_2\text{O}$$

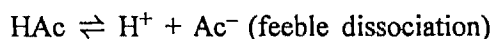
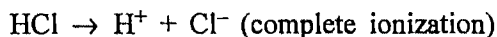
Discussion :

- The two oxidizing agents commonly used for the generation of MnO_4^- are ammonium persulfate in phosphoric acid – nitric acid medium in the presence of a little silver nitrate as catalyst, and potassium periodate. The merits of the periodate method include:
 - The concentration of the acid has little influence and may be varied within wide limits
 - The boiling may be prolonged beyond the time necessary to oxidize Mn(II) without detriment
- The test solution must contain < 20 ppm of manganese, otherwise the colour will be too dark.
- If chlorides are present it is necessary to evaporate with a mixture of nitric and sulfuric acids until fumes of the latter appear as chlorides react with the periodate. Other reducing substances reacting with periodate or permanganate must be destroyed similarly before the periodate oxidation.

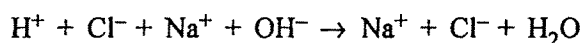
Experiment No. 2: Conductometric Titration: HCl-CH₃COOH mixture and dibasic acid.

Theory :

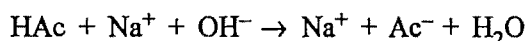
The conductance of a mixture of HCl and CH₃COOH is essentially due to that of HCl alone, since the dissociation of CH₃COOH (a weak electrolyte) is almost completely suppressed by the presence of the common ion H⁺ released from the strong acid HCl :



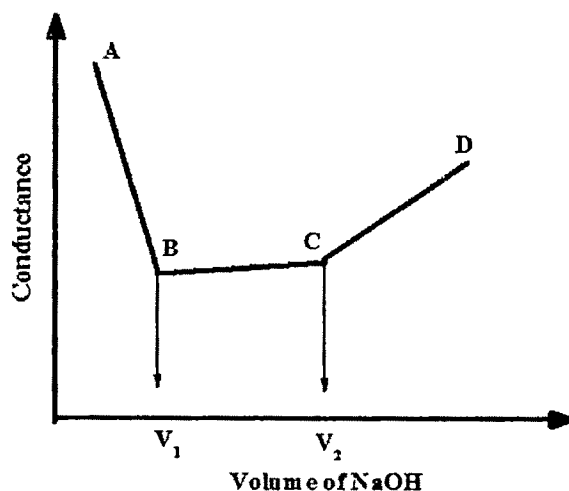
The ion conductance of H⁺ is very high and so, when H⁺ ions are removed from solution and replaced by Na⁺ of low ion conductance there will be a fall in conductance. This happens when NaOH is added to the mixture and neutralization occurs:



After complete neutralization of HCl, CH₃COOH remains in solution and is weakly dissociated. The further addition of NaOH neutralizes CH₃COOH to produce Na⁺ and CH₃COO⁻ ions, leading to an increase in conductance :



After all the CH₃COOH is used up, addition of further NaOH leads to increase in concentration of Na⁺ and the highly conducting ion OH⁻. The conductance of the solution increases very sharply. The conductance versus volume (or, number of drops) of NaOH plot consists of three straight lines : AB, BC and CD with two break points B and C.



Here, V₁ corresponds to volume of NaOH required to neutralize HCl and (V₂ - V₁) corresponds to that required to neutralize CH₃COOH. Knowing the strength of NaOH, the strength of HCl and CH₃COOH in the mixture can be found out using the law of equivalents (V_AS_A = V_BS_B).

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For a dibasic acid like $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid), where the first dissociation is like that of a strong acid and the second dissociation is weak, e.g.,



the neutralization plot is similar to that discussed above. The additional feature in this case is the restriction $V_1 = V_2 - V_1$ i.e., $V_2 = 2V_1$, because the acid is dibasic.

Procedure :

- 1) Prepare 100 ml (~N/5) oxalic acid solution in a 100ml volumetric flask by accurate weighing of solid oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) using a digital balance.
- 2) Take the supplied (~N/2) NaOH solution in a burette and determine the volume for 50 drops of NaOH to calculate the volume of one drop of NaOH.
- 3) Standardize the supplied NaOH solution against the prepared primary standard oxalic acid solution using an aliquot of 25 ml, and phenolphthalein as indicator.
- 4) Pipette out 10 ml of the primary standard oxalic acid in a clean beaker, add sufficient quantity of distilled water and then dip the conductivity cell. Standardize the conductivity meter. Measure the conductance of this solution. Titrate the mixture conductometrically by adding NaOH dropwise from the burette. Draw a graph of conductance versus number of drops of NaOH. Determine strength of NaOH and compare it with that obtained from analytical procedure.
- 5) Take 10 ml of the supplied strong acid-weak acid mixture, (or a dibasic acid like oxalic/succinic acid) and follow an identical procedure (as outlined above) for the conductometric titration using NaOH as the titrant. Find individual concentration of HCl and CH_3COOH (or that of dibasic acid) using the graphical plot.

NOTE : Conductometric titration of (i) HCl vs NaOH and (ii) CH_3COOH vs. NaOH need to be carried out before the conductometric titration of the HCl- CH_3COOH mixture.

Useful Physical Constant

For CH_3COOH , $K_a = 1.753 \times 10^{-5}$ (at 298 K)

Ion conductance at infinite dilution : (at 298 K) (in $\text{ohm}^{-1} \text{ cm}^2 \text{ g-eqv}^{-1}$ unit)

$\lambda(\text{H}^+) = 349.92$, $\lambda(\text{CH}_3\text{COO}^-) = 40.9$, $\lambda(\text{Na}^+) = 50.11$, $\lambda(\text{Cl}^-) = 76.34$, $\lambda(\text{OH}^-) = 198.0$.

Temperature correction :

$\lambda_t = \lambda_{25} [1 + \alpha (t - 25)]$, where t is the temperature in $^\circ\text{C}$

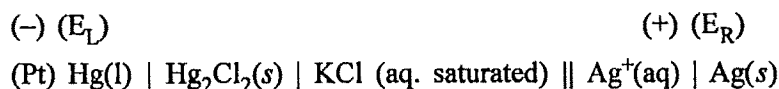
$\lambda = 0.0142$ for H^+ ;

= 0.016 for OH^- ;

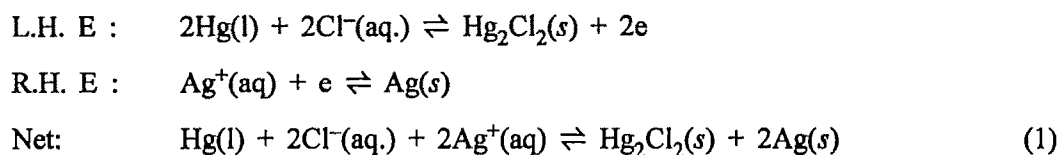
= 0.02 for other anions.

Experiment No. 3 : Potentiometric Titration – Halide Ion Estimation.**Theory :**

When the $\text{Ag}^+/\text{Ag}(s)$ redox electrode is coupled with a saturated calomel electrode (SCE), the following electrochemical cell is produced:



where, the symbol \parallel stands for 2(M) agar – KNO_3 salt-bridge, which minimizes the liquid junction potential. The half cell reactions at the electrodes are:



The overall cell reaction is given by (1) and the e.m.f. of the cell is given by:

$$\begin{aligned} E_{\text{Cell}} &= E_R - E_L = E_{\text{Ag}^+/\text{Ag}} - E_{\text{SCE}} \\ E_{\text{Ag}^+/\text{Ag}} &= E_{\text{Ag}^+/\text{Ag}}^0 + 0.059 \log[a_{\text{Ag}^+}/a_{\text{Ag}(s)}], \text{ at } 25^\circ\text{C} \end{aligned} \quad (1a)$$

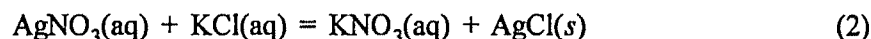
$\text{Ag}(s)$, being in the standard state, will have unit activity. For a dilute solution, activity (a) of Ag^+ ion may be replaced by the numerical value of its concentration $[\text{Ag}^+]$. Thus,

$$E_{\text{Cell}} = E_{\text{Ag}^+/\text{Ag}}^0 + 0.059 \log [\text{Ag}^+] - E_{\text{SCE}} \quad (1b)$$

Since $E_{\text{Ag}^+/\text{Ag}}^0$ and E_{SCE} are fixed, E_{cell} depends on $[\text{Ag}^+]$.

The standard reduction potential of an electrode may be defined as the emf of the cell produced by coupling standard hydrogen electrode on the left and the electrode under consideration on the right with all reactants and products at unit activities.

As KCl solution is added to AgNO_3 solution, the following reaction takes place:



AgCl being sparingly soluble, $[\text{Ag}^+]$ decreases as more and more KCl solution is added, resulting in a decrease of E_{Cell} with increase in the number of drops (n) of KCl solution. Near the equivalence point, addition of a small volume (1 drop) of KCl solution removes practically all the Ag^+ ions from the solution. This produces an abrupt decrease in E_{cell} and the $\Delta E_{\text{cell}}/\Delta n$ value is also very large.

From the plot of E_{cell} vs. volume or number of drops (n) of KCl solution, it is possible to find the volume (V) or the number of drops (n) of KCl required to completely precipitate

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the Ag^+ ions present in the solution, and the value of E_{cell} at the equivalence point. The derivative plot $|\Delta E_{\text{cell}} / \Delta n|$ vs. n shows a maximum at the value of n corresponding to the equivalence point. The strength of the AgNO_3 solution may now be calculated using the relation:

$$V(\text{AgNO}_3) \times S(\text{AgNO}_3) = V(\text{KCl}) \times S(\text{KCl}) \quad (3)$$

Thus, from potentiometric titration the strength of an unknown AgNO_3 solution may be determined.

If the halide ion concentration of an unknown solution is to be determined, the same procedure may be repeated, and with $S(\text{AgNO}_3)$ determined. The strength of an unknown halide ion is determined using a separate plot and using eqn. (3)

Procedure :

1. Prepare an agar KNO_3 salt bridge.
2. Prepare 100 ml of (N/100) AgNO_3 solution in distilled water.
3. Prepare 100 ml of a standard (N/10) KCl solution in distilled water by accurate weighing, using a digital balance.
4. Take 10 ml of the prepared AgNO_3 solution in a 100 ml beaker and dip the silver electrode in this solution. Add sufficient amount of distilled water so that the electrode dips properly.

This constitutes the experimental electrode $\text{Ag}^+ / \text{Ag}(s)$.

5. Set up the experimental cell by connecting the saturated calomel electrode (SCE) and the experimental electrode through the agar- KNO_3 salt bridge.
6. Take the prepared KCl solution in a burette and determine the volume of 50 drops and then calculate the volume of 1 drop of KCl .
7. Connect the experimental cell with the standardized potentiometer.
8. Measure the e.m.f. of the cell E_{cell} . Add 2-drops of (N/10) KCl solution, stir gently and record the E_{cell} . Repeat the procedure till 10 drops of titrant are added. Then add 1 drop at a time till the equivalence point is reached, which is indicated by a sharp decrease of E_{cell} . Take a few more readings beyond the equivalence point.
9. Plot (i) the observed E_{cell} values against number of drops of KCl solution added, (ii) $|\Delta E_{\text{cell}} / \Delta n|$ versus n . Determine the equivalence point and the E_{cell} value at the equivalence point from the graph. Repeat the procedure using unknown KCl solution.
10. Calculate the strength of the AgNO_3 solution by using the volume of standard KCl solution required at equivalence point (obtained graphically). Then determine the strength of unknown halide ion from the second plot.

Experiment No. 4 : pH-metric Titration – monobasic acid.**Theory :**

The pH of an aqueous solution can be measured using glass–calomel electrode system in which following electrochemical cell is formed :

Ag | AgCl(s) | 0.1(M)HCl | Glass | Solution of unknown pH | Saturated Calomel electrode

The right hand electrode is the saturated calomel electrode (SCE) and the left hand electrode is the glass electrode which is actually an ion selective membrane electrode, reversible with respect to H^+ ion. The glass electrode is the most likely used hydrogen ion responsive electrode and its use depends on the fact that when a glass membrane is immersed in a solution, a potential is developed which is a linear function of the hydrogen ion concentration of the solution. The internal HCl solution is maintained at constant concentration, the potential of the silver-silver chloride electrode inserted into it will be constant, and so too will the potential between HCl solution and the inner surface of the glass bulb. Hence the only potential which can vary is the potential between the outer surface of the glass bulb and the test solution in which it is immersed, so the overall potential of the electrode is governed by the hydrogen ion concentration of the test solution. Glass electrodes are also available as combination electrodes, which contain the indicator electrode and a reference electrode combined in a single unit. The potential (E_g) of the glass electrode at $25^\circ C$ may be expressed as

$$\begin{aligned} E_g &= E_g^0 + 0.059 \log a_{H^+} \\ &= E_g^0 - 0.059 \text{ pH} \end{aligned} \quad (1)$$

For actual pH measurement, the glass electrode is standardized in buffer solutions of known pH values.

Ionisation of a weak monobasic (HA) in aqueous solution may be represented as,



where the ionisation constant (K_a) is given by the activity quotient of the ionisation equilibrium (2),

$$K_a = a_{H^+} a_{A^-} / a_{HA} \quad (3)$$

Here a represents activity of the respective species which is related to the molar concentration, (c) according to $a = c.f.$, where f = activity coefficient. In dilute aqueous solutions of weak acids, ionic strength is very low, so the activity coefficients approach unity, hence, the concentrations approach activities. Consequently the ionization constant (K_a) may be expressed as

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$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (4)$$

When a strong base (NaOH) is added to a weak acid (acetic acid) in an amount less than the stoichiometric requirement a buffer solution is formed whose pH is given by the Henderson's equation.

$$pH = pK_a + \log_{10} \frac{[Salt]}{[Acid]}$$

A pH metric titration curve may be constructed by plotting the pH of the acid solution after each addition of the strong base versus the number of drops of alkali (n). The equivalence point of the titration may be determined graphically. The derivative plot $[|\Delta pH / \Delta n| \text{ vs. } n]$ shows a maximum at the value of n corresponding to the equivalence point.

Procedure :

1. Prepare 100 ml of a standard (N/20) solution of oxalic acid by accurate weighing in a digital balance.
2. Prepare 100 ml of (\sim N/2) NaOH solution.
3. Prepare 100 ml of (\sim N/20) acetic acid solution.
4. Prepare standard buffer solution of pH = 4 and pH = 7 by dissolving the corresponding pH tablets in the specified volume of distilled water.
5. Standardize the pH meter by alternately dipping the glass-calomel electrode assembly in pH = 4 and pH = 7 buffer solutions and adjusting the instrument accordingly at the experimental temperature.
6. Determine the volume of 50 drops of the titrant solution and calculate the volume of one drop.
7. Take 25 ml of (N/20) acetic acid solution in a 100 ml beaker. Add sufficient quantity of distilled water so that the combined electrode (glass-calomel assembly) dips into it properly. Allow the system to attain the equilibrium at the experimental temperature and record the pH.
8. Add 2 drops of the (N/2) NaOH solution from a burette / micro burette stir gently to mix uniformly and record the pH. Repeat the process until the pH of the solution reads \sim 4.5. Then add 1 drop each time till the equivalence point is reached (indicated by sharp rise in pH). Record the pH and the number of drops of the titrant in a tabular form. Take a few more readings beyond the end point.

NOTE : The same experiment may be carried out by coupling a Quinhydrone electrode (reversible with respect to H^+ ion) with a saturated calomel electrode.

Experiment No. 5: Ion-exchanger — Cation content of a sample by cation exchanger

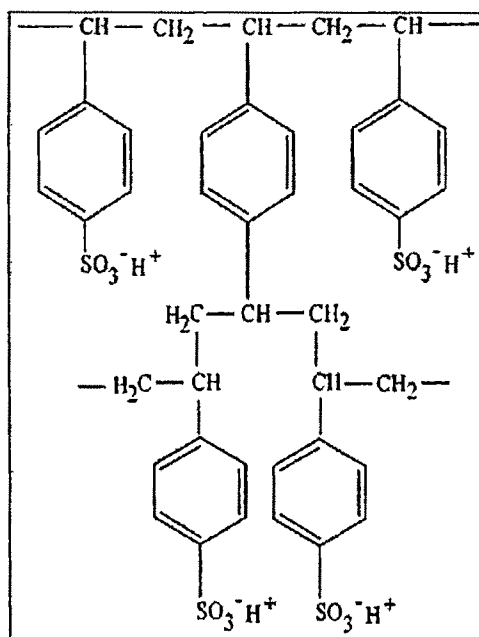
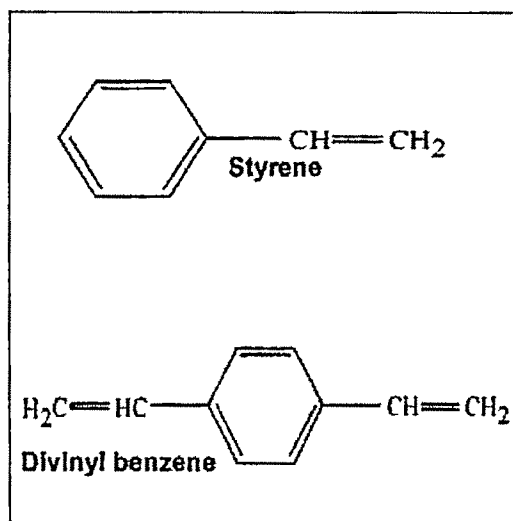
The term ion exchange is generally understood to mean the exchange of ions of like sign between a solution and a solid, highly insoluble body in contact with it. The solid i.e. the ion exchanger must contain ions of its own, and for the exchange to proceed sufficiently rapidly and extensively, the solid must have an open, permeable molecular structure so that ions and solvent molecules can move freely in and out. Many substances, both natural (e.g., certain clay materials) and artificial, have ion exchanging properties. But for analytical purpose synthetic organic ion exchangers are of chief interest. All ion exchangers of value in analysis have several properties in common: they are almost insoluble in water and in organic solvents, and they contain active or counter ions that will exchange reversibly with other ions in a surrounding solution without any appreciable physical change occurring in the material. The ion exchanger is of complex nature and is polymeric. The polymer carries an electric charge that is exactly neutralized by the charges of the counter ions. These active ions are cations in a cation exchanger and anions in an anion exchanger. Thus a cation exchanger consists of a polymeric anion and active cations, while an anion exchanger is a polymeric cation with active anions. We may define a cation exchange resin as a high molecular weight, cross – linked polymer containing sulphonic, carboxylic, phenolic, etc., groups as an integral part of the resin and an equivalent amount of cations; an anion exchange resin is a polymer containing amine (or quaternary ammonium) groups as integral parts of the polymer and an equivalent amount of anions such as chloride, hydroxyl or sulphate ions.

The fundamental requirements of a useful resin are:

1. The resin must be sufficiently cross-linked to have only a negligible solubility.
2. The resin must be sufficiently hydrophilic to permit diffusion of ions through the structure at a finite and usable rate.
3. The resin must contain a sufficient number of accessible ionic exchange groups and must be chemically stable.
4. The swollen resin must be denser than water.

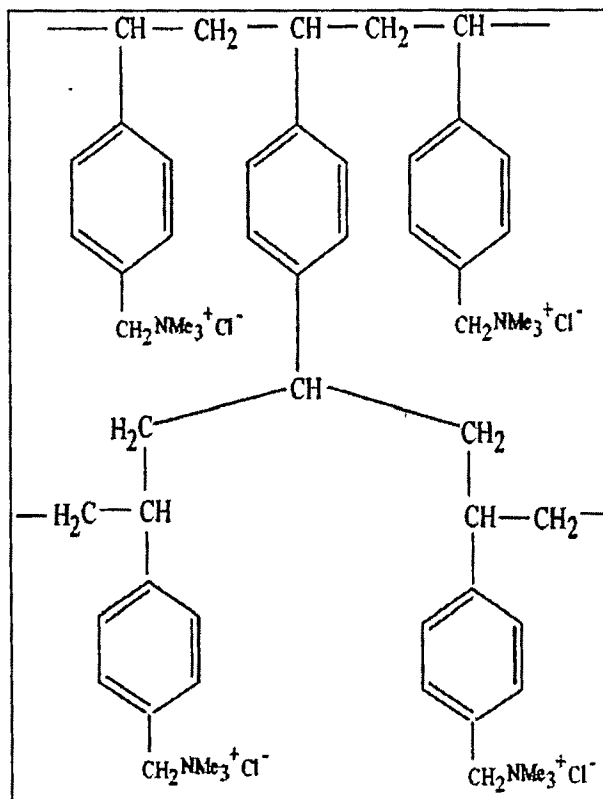
A widely used cation exchange resin is that obtained by the copolymerization of styrene and a small proportion of divinyl benzene followed by sulphonation. The structures may be represented as follows:

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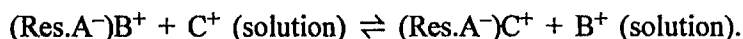


Cation exchange resin

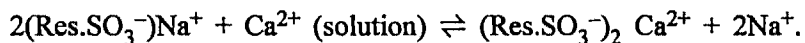
Commonly used anion exchange resin is prepared by copolymerization of styrene and a little divinylbenzene, followed by chloromethylation (introduction of the $-\text{CH}_2\text{Cl}$ group) and interaction with a base such as trimethylamine. It may be represented as follows:



Action of ion exchange resins: Cation exchange resins contain free cations which can be exchanged for cations in solution.

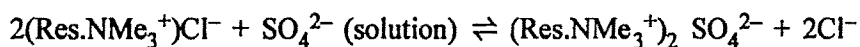


If the experimental conditions are such that the equilibrium is completely displaced from left to right then the ion C^+ will be completely fixed on the cation exchanger. A typical example is the displacement of sodium ions in a sulphonate resin by calcium ions:



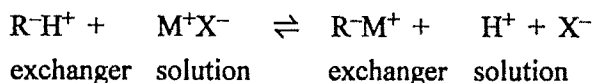
The reaction is reversible; by passing a solution containing sodium ions through the product, the calcium ions may be removed from the resin and the original sodium form regenerated.

A typical reaction of an anion exchange resin may be represented as:



Determination of Na^+/K^+ in a given solution by ion exchange method

Principle : When known volume of a solution containing Na^+ or K^+ ion in the form of their salts with strong acids is passed through a column of cation exchange resin in H^+ - form, an equivalent amount of H^+ ion is released and the metal ion (Na^+ or K^+) is held by the resin:



The liberated acid in the effluent may be estimated by titrating with a standard solution of NaOH. Therefore, $(\text{Na}^+ \text{ or } \text{K}^+) \equiv \text{H}^+ \equiv \text{OH}^-$

and, 1000 ml of (N) NaOH \equiv 22.99 g of $\text{Na}^+ \equiv$ 39.10 g of K^+

Chemicals and apparatus required :

- a) Standard (N/50) oxalic acid solution :

To be prepared by accurate weighing (0.315 g/250 ml solution in distilled water)

- b) (\sim N/50)NaOH solution: 0.3 – 0.5 g of (A.R.) NaOH / 250 ml solution in distilled water
c) Cation exchange resin: Dowex – 50 or Amberlite IR – 120 or Zeolit – 225 (50 – 100 or 15 – 50 mesh)
d) Methyl red indicator: 0.1 – 0.2 % solution in 60% ethanol
e) 2(M) HCl (A.R.) solution
f) (A.R.) NaCl/KCl or $\text{NaNO}_3/\text{KNO}_3$: \sim 0.2 – 0.4 g of the salt/100 ml of solution in distilled water to prepare (\sim M/50) solution

Procedure :

1. Plug the ion exchange column (15 cm x 1 cm) at its bottom with glass wool and attach a rubber tubing with a pinch cock for adjusting the rate of flow.
2. Place \sim 10 – 15 g of the dry resin in a beaker and add 50 ml of 2(M) HCl and stir thoroughly, allow to stand for \sim 30 minutes. By this time the swelling of the resin will be complete and will be converted to its H^+ - form.
3. Partly fill the ion-exchange column with distilled water. Remove any air bubble that may adhere to the glass wool plug or to the wall of the tube.
4. Insert the resin into the column by washing with water, and drain out the water inside the tube as required. Adjust the height of the resin in such a way that there remains sufficient space at the top of the column for holding \sim 15 – 20 ml of liquid. Keep the resin head always covered with water.
5. Wash the resin with \sim 100 ml of distilled water, adding \sim 10 ml at a time, keeping the resin top always under the liquid. Test the effluent occasionally using methyl red

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indicator solution. When 10 drops of effluent does not impart any red color to the indicator solution, the resin column may be considered acid free and ready for exchange. Close the stopper.

6. Place a 250 ml conical flask under the column for collecting the effluent. Place 10 ml of the test solution [which is $\sim (M/50)$ in Na^+ or K^+] on the top of the column using a pipette. Release the stopper and adjust the rate of flow $\sim 15 - 20$ drops per minute.
7. When the level of the experimental solution just approaches the resin top, start washing the column with distilled water adding 10 ml at a time, always keeping the resin covered with water. Test the effluent with methyl red indicator solution after 5 – 6 washings. If a red color is imparted, add the red solution quantitatively into the main bulk of the effluent. Continue the process of washing with water and testing with methyl red indicator solution till 10 drops of the effluent do not impart red color to the methyl red indicator solution. Close the stopper.
8. Titrate the combined effluent and the washings with standard ($\sim N/50$) NaOH solution using methyl red indicator till the red color of the solution changes to yellow. Record the titre (V).
9. Standardization of NaOH solution:
Take an aliquot of 10 ml of the standard ($N/50$) oxalic acid solution in 250 ml conical flask, dilute to ~ 100 ml with distilled water, add 2–3 drops of phenolphthalein indicator and titrate with ($\sim N/50$) NaOH solution till the color changes to red. Record the titre (V').
10. After the experiment is over, pass 100 ml of 2(M) HCl through the column to regenerate the H^+ - form of the resin for future use. Wash with distilled water as before to remove any free acid from the column and close the stopper. The resin top should be always kept under water.
11. Calculate the total quantity of Na^+/K^+ in the sample.

Calculation :

Strength of oxalic acid solution = $(w/0.315) (N/50)$, where w = weight of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 250 ml solution.

$$\text{Strength of NaOH solution} = \frac{10w}{0.315V'} (N/50).$$

Therefore, 10 ml of sample solution = V ml of $\frac{10w}{0.315V'} (N/50)$ NaOH solution

$$= \frac{10w}{0.315V'} \frac{V}{50} \text{ ml of (N) NaOH solution.}$$

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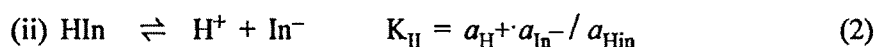
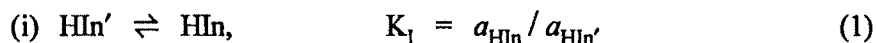
$$\begin{aligned}
 \text{So, 100 ml sample solution} &\equiv \frac{100w}{0.315V} \frac{V}{50} \text{ ml of (N) NaOH solution} \\
 &\equiv 0.1459 \frac{wV}{V'} \text{ g of Na}^+ \\
 &\equiv 0.2481 \frac{wV}{V'} \text{ g of K}^+.
 \end{aligned}$$

Experiment No. 6 : To determine the pK_{In} value of an acid-base indicator by colourimetric method.

Theory :

Acid-base indicators are either weak organic acids or bases having distinctly different colours in acidic and alkaline solution, and by virtue of change of colour they indicate the end points of acid-base titrations. Such indicators exist in two tautomeric forms. One of the tautomers is non-ionizable but the other is an electrolyte and hence ionizable. The colours of the two tautomeric forms are different. The colour of the ion is the same as that of the tautomer from which it is produced.

Let us consider an acidic indicator acid like bromocresol-green. Let HIn' be the non-ionizable tautomeric form and HIn be the ionizable form, while In^- represents the indicator ion. The colour of HIn and In^- is the same but different from that of HIn' . In aqueous solution there would exist two equilibria,



In acidic solutions, the dissociation will be suppressed; practically the whole of the indicator shall remain in undissociated form HIn' , if the equilibrium constant K_I of equation (1) is small. Multiplying equations (1) and (2):

$$K_{In} = a_{H^+} \cdot a_{In^-} / a_{HIn'} \quad (3)$$

In dilute solution, the activities may be replaced by concentrations,

$$\text{So,} \quad K_{In} = [H^+] \cdot [In^-] / [HIn'] \quad (4)$$

Transforming equation (4) in logarithmic form one obtains,

$$pH = pK_{In} + \log_{10}[In^-] / [HIn'] \quad (5)$$

(where $pK_{In} = -\log_{10}K_{In}$ and $pH = -\log_{10}[H^+]$ in dilute solution)

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Thus, if a fixed amount of the indicator is placed in the same volume of a series of buffer solutions of different known pH values, the ratio, $[\text{In}^-]/[\text{HIn}]$, will increase with increase of pH. If the values of the ratio at different pH are determined by measuring the colour intensity of the indicator solutions, then the pK_{In} value of the indicator can be found out if the pH of the buffer solutions is known.

If the alkaline form of the indicator (In^-) absorbs at a selected wave length and Beer's Law is obeyed in the range of the concentration of the indicator used, then the absorbance (A) of the indicator solution at a particular pH will be proportional to its concentration, provided the acid form (HIn') does not absorb at this wave length.

$$A = \epsilon.[\text{In}^-].l \quad (6)$$

In a strongly alkaline solution, HIn is practically absent, and the absorbance (A') will correspond to the total concentration (T_{In}) of the indicator.

$$A' = \epsilon.T_{\text{In}}.l \quad (7)$$

where ϵ = molar extinction coefficient of In^- and l = optical path length in cm. Mass balance equation of the indicator is,

$$T_{\text{In}} = [\text{HIn}'] + [\text{In}^-] \quad (8)$$

$$[\text{HIn}'] = T_{\text{In}} - [\text{In}^-]. \quad (8a)$$

$$\text{From (7) - (6) one obtains } (A' - A) / \epsilon.l = [\text{HIn}']. \quad (9)$$

$$\text{From (6) one obtains } A/\epsilon.l = [\text{In}^-] \quad (9a)$$

Substituting these values of $[\text{HIn}]$ and $[\text{In}^-]$ in equation (5), one obtains

$$\text{pH} = \text{pK}_{\text{In}} + \log_{10}[A / (A' - A)] \quad (10)$$

A and A' may be measured colorimetrically. Therefore, by plotting pH against $\log_{10}[A/(A'-A)]$ of the buffer solutions, a straight line of slope = 1 will be obtained, of which the intercept on the pH axis will give pK_{In} .

Procedure : (for bromocresol green indicator)

1. Prepare 100 ml. of exact 0.4 (N) acetic acid ($\text{pK}_{\text{a}} = 4.74$ at 25°C) and 100 ml. of exact 0.4 (N) NaOH solutions separately by usual procedure.
2. Take 12 hard glass test tubes and label them from 1 to 12. Prepare the following series of solutions by proper mixing (experimental pH values may be obtained from chart below).

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Test tube	Vol. of 0.4 (N) Acetic acid (ml.)	Vol. of 0.4 (N) NaOH (ml.)	Vol. of water (ml.)	pH (experimental)
1.	5.0	0.5	4.5	3.72
2.	5.0	1.0	4.0	4.05
3.	5.0	1.5	3.5	4.27
4.	5.0	2.0	3.0	4.45
5.	5.0	2.5	2.5	4.63
6.	5.0	3.0	2.0	4.80
7.	5.0	3.5	1.5	4.99
8.	5.0	4.0	1.0	5.23
9.	5.0	4.5	0.5	5.57

In test tube numbers 10 to 12, take 2.5 ml. of 0.4(N) NaOH and add 7.5ml. of water.

3. Add 2-3 drops of bromocresol green to test tube 10. Set the spectrophotometer at 570nm, adjust the transmittance of water to 100%. Measure the transmittance of the solution. Adjust the number of drops of the indicator (if necessary) in test tube no. 11/12 so that the transmittance lies approximately in the range 15% -25%.
4. Add the same number of drops of the indicator to all 9 buffer solutions and measure the transmittance of all such solutions and calculate absorbances using the relation $A = 2 - \log_{10}(\%T)$.
5. Plot pH vs. $\log_{10}[A / (A'-A)]$ and determine slope and intercept of the plot.

NB : Preparation of bromocresol green

1g of indicator is triturated in a clean glass mortar with 14.4 ml of 0.1(M) NaOH solution and then diluted with water to 1L (in a volumetric flask).

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Experiment No 1: Determination of surface tension of a given solution by drop weight method using a stalagmometer.

Theory :

In a liquid, the molecules attract one another. As a result of this intermolecular attraction, a molecule in the bulk of the liquid suffers zero resultant force, whereas, a molecule at the surface suffers a net resultant force of attraction towards the bulk. The surface of a liquid behaves as a stretched membrane and liquids at rest possess a physical property called surface tension. *Surface tension* of a liquid at a particular temperature is defined as the force acting tangentially across the surface and at right angles to any line of unit length on it. The surface tension may alternatively be defined as the work done in increasing the surface area of the liquid by unity. The unit of surface tension is dyn cm^{-1} (c.g.s.) or, N m^{-1} (SI). Surface tension of a liquid depends upon temperature, it decreases as temperature increases and vanishes at the critical temperature of the liquid.

The basis of determining surface tension (γ) of a liquid using a stalagmometer is as follows. When a liquid flows slowly out of the orifice of a capillary tube under the action of gravity, the balance of force just at the point of detachment of the spherical drop may be expressed by equation (1) (neglecting the buoyancy effects of surrounding air medium)

$$mg = 2\pi r\gamma\phi, \quad (1)$$

where m = mass of a drop, g = acceleration due to gravity, r = radius of the capillary, γ = surface tension of the liquid, ϕ = Harkins-Brown correction factor for the instrument.

If a definite volume (V) of two liquids (1 and 2) of density d_1 and d_2 and surface tension γ_1 and γ_2 on passing through a uniform capillary tube (stalagmometer) produces respectively n_1 and n_2 number of drops, $m_1 = (V/n_1)d_1$ and $m_2 = (V/n_2)d_2$ and hence

$$\frac{\gamma_1}{\gamma_2} = \frac{(V/n_1)d_1}{(V/n_2)d_2} = \frac{n_2 d_1}{n_1 d_2} \quad (2)$$

Thus, by counting the number of drops produced from a fixed volume of two liquids and determining the ratio of their densities one may compare their surface tensions. If the surface tension of one of the liquids, (reference liquid, e.g. water) is known (γ_w), then the surface tension (γ_L) of another liquid can be obtained using the relation

$$\frac{\gamma_L}{\gamma_w} = \frac{n_w d_L}{n_L d_w} = \frac{n_w}{n_L} S_L, \quad (3)$$

where S_L = specific gravity of the liquid. So,

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$$\gamma_L = \frac{n_w}{n_L} S_L \gamma_w \quad (4)$$

Thus, by counting the number of drops produced by passing a definite volume of water and the liquid, or, solution and determining its specific gravity, surface tension of the liquid (γ_L) can be determined provided (γ_w) of water at the same temperature is known.

Effect of additives – (a) NaCl, KCl etc.: surface tension increase slightly.

(b) HOAc, C₂H₅OH etc.: surface tension decreases.

Procedure :

1. Determine the specific gravity (S_L) of the solution/liquid by usual procedure (using specific gravity bottle).
2. Rinse the stalagmometer with distilled water thoroughly. Suck in fresh distilled water and adjust the number of drops falling per minute between 10 and 15. Suck in water again, release and start counting the number of drops as the meniscus touches the upper graduation mark and stop when it touches the lower mark. Repeat the counting and record the average number of drops (n_w).
3. Repeat the process (2) with the supplied solution/liquid and record the average number of drops (n_L).
4. Calculate the surface tension of the solution using the relation (4).

Experiment No 2 : Determination of viscosity coefficient of a given solution with Ostwald viscometer.

Theory :

Viscosity is the property which opposes the relative motion of adjacent layers of a liquid and can be regarded as a type of internal friction. *Newton's law* of viscous force is applicable when a liquid flows slowly and executes streamline motion. The law states that, the force (f) required to maintain a velocity difference of dV_x (in the x-direction) between two parallel layers of area, A , separated by a distance of dz in the z-direction) is given by

$$f = \eta A \frac{dV_x}{dz} \quad (1)$$

where η is the *viscosity coefficient* of the liquid which is defined as the force per unit area required to maintain a unit velocity gradient (in the x-direction). The (c.g.s.) unit of η is *poise* and 1 poise = 1 dyne sec cm⁻². The magnitude η of depends on temperature. η decreases by about 2% per degree Celsius rise in temperature.

The viscosity coefficient (η) may be determined experimentally using an Ostwald viscometer which utilizes the Poiseuille's equation,

$$\eta = \frac{\pi r^4 t P}{8 V l} \quad (2)$$

This equation is valid for an incompressible fluid (i.e. a liquid) flowing very slowly (streamline motion) through a narrow tube of radius, r , and length, l , under an average pressure of P , when there is a flow of V volume of the liquid in time t .

If t_1 and t_2 be the times of fall of a definite volume of two liquids (1 and 2) through the same Ostwald viscometer and η_1 and η_2 be their viscosity coefficients, and P_1 and P_2 respectively be the average pressures, then one may obtain from eqn. (2).

$$\frac{\eta_1}{\eta_2} = \frac{P_1 t_1}{P_2 t_2} \quad (3)$$

The pressure P , driving the liquid through the capillary at any instant, is equal to $h d g$, where h is the difference in height between the levels of the liquid in the two limbs, d is the density of the liquid and, g is the acceleration due to gravity. During the experiment, P decreases with time as h decreases. The initial height difference (h_1) and the final height difference (h_2), ($h_1 > h_2$), are same for both the liquids, since the same volume of the two liquids are allowed to pass through the capillary tube. Thus, the average pressures P_1 and P_2 may be expressed as :

$$P_1 = [(h_1 + h_2) / 2] d_1 g$$

$$\text{and} \quad P_2 = [(h_1 + h_2) / 2] d_2 g$$

Thus,

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad (4)$$

In the Ostwald viscometer, a definite volume of a reference liquid (water) is introduced in the wider arm of the instrument. The liquid is sucked into the narrower arm and the time required for a fixed volume of the liquid to flow through the capillary under the action of gravity is noted. The procedure is repeated for the experimental liquid (L).

When water (w) is used as the reference liquid, the expression (4) is transformed to (5).

$$\frac{\eta_L}{\eta_w} = \frac{d_L}{d_w} \left(\frac{t_L}{t_w} \right) = S_L \left(\frac{t_L}{t_w} \right) \quad (5)$$

$$\eta_L = S_L \left(\frac{t_L}{t_w} \right) \eta_w \quad (6)$$

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where, η_w , η_L , d_L , t_w , t_L , have their usual meaning and S_L is the specific gravity of the liquid. Thus, if the viscosity coefficient (η_w) of water is known, the viscosity coefficient (η_L) of the liquid can be determined by determining the specific gravity (S_L) of the liquid and measuring the times of flow t_w and t_L of a definite volume of water and the liquid respectively. Additives like ethanol, glycerol or cane sugar increase the viscosity coefficient.

Procedure :

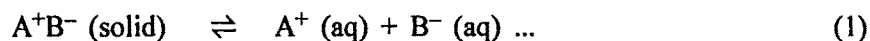
1. Determine the specific gravity of the supplied solution/liquid by usual procedure (using a specific gravity bottle).
2. Rinse the Ostwald's viscometer with distilled water and drain out the water thoroughly. Add a measured volume of water (using a pipette) into the wider limb of the viscometer and clamp it vertically. Suck the water, in the narrower limb, release it and start the stopwatch as the meniscus touches the upper mark of the narrower limb. Stop the stopwatch as the meniscus touches the lower mark of the same limb. Repeat the process and record the average time of flow.
3. Repeat the process 2 with the supplied solution/liquid and calculate the viscosity coefficient of the supplied solution/liquid using equation (6).

Experiment No 3 : Determination of solubility and solubility product of a sparingly soluble salt in water, and in various electrolytic media by titrimetric method.

Theory :

Solubility of a solute in a solvent at a particular temperature is defined as the number of grams of the solute required to saturate 100 grams of the solvent to produce a saturated solution that remains in equilibrium with undissolved solute. If S_0 be the solubility, then the concentration of the saturated solution is $10 S_0/M$ molal where M is the molar mass of the solute. Saturated solutions of sparingly soluble salts are sufficiently dilute; as such the concentrations in molarity are very close to molality. For such solutions molar concentrations may conveniently be used as the measure of their solubilities.

Solubility product of a sparingly soluble electrolyte is the product of the activities of the ions (raised to proper power), in a saturated solution at a particular temperature. Solubility equilibrium of a 1 : 1 sparingly soluble salt, A^+B^- , in aqueous medium may be represented according to :



for which the activity solubility product (K_a) and the concentration solubility product (K_c) are defined as

$$K_a = a_{A^+} \times a_{B^-} \quad (1a)$$

$$K_c = [A^+] \times [B^-] \quad (1b)$$

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Where a represents activity and $[]$ represents molar concentration of the aquated ions.

Since, activity (a) = concentration \times activity coefficient, i.e.,

$$a_{A^+} = [A^+]f_{A^+} \text{ and } a_{B^-} = [B^-]f_{B^-}$$

$$\therefore K_a = K_c(f_{A^+}f_{B^-}) = K_c(f_{\pm})^2 \quad (1c)$$

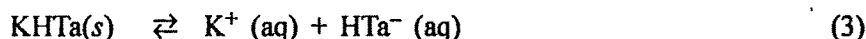
here, (f_{\pm}) is the mean ionic activity coefficient of the electrolyte.

As the saturated solution of a sparingly soluble salt is very dilute, the activities of the ions become numerically equal to their molar concentrations since the mean activity coefficient (f_{\pm}) tends to unity, therefore,

$$K_a = K_c = S_0 \times S_0 = S_0^2 \quad (2)$$

where, S_0 = solubility of the salt (A^+B^-) in mole per litre in water.

Potassium hydrogen tartarate (KHTa) is a sparingly soluble salt. In aqueous solution it ionises according to,



If the concentration of HTa^- ion in the saturated solution of KHTa in water at room temperature is S mole/litre, then the concentration solubility product, K_c , may be obtained from the relation :

$$K_c = S^2 \quad (4)$$

Solubility (S') of the salt (KHTa) in a solution containing an electrolyte which carries a common ion (e.g. KCl), is lower than that in pure water. Since the solubility product (K_a) is a constant,

$$K_a = K_c = (S' + C) S' \quad (5)$$

where, C , is the concentration of the electrolyte (KCl). In the presence of an electrolyte having no ions in common (eg. NaNO_3), the ionic strength of the medium increases, and the mean ionic activity coefficient decreases (a consequence of *Debye-Hückel limiting law*) and there is a consequent increase of solubility (S) of the sparingly soluble salt (cf. eq. 1c). As a result, K_c increases since K_a at a particular temperature remains unchanged.

Procedure :

1. (a) Prepare 250 ml of standard (N/20) oxalic acid solution by accurate weighing. Prepare 250 ml of approximately (N/20) NaOH solution and standardise the same against the standard (N/20) oxalic acid solution using phenolphthalein as indicator.
(b) Prepare 100 ml of (N/20) KCl and 100 ml (N/20) NaNO_3 by accurate weighing.
2. In a clean and dry 250 ml stoppered glass bottle take ~ 1.5 g. of the salt (KHTa) and 100 ml of distilled water. Shake the bottle till equilibrium is reached and a saturated solution is obtained. Check that some solid remains undissolved. If necessary add some more solid and shake.

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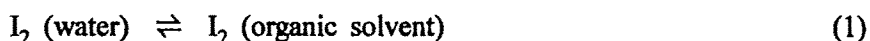
3. Perform step (2) using the solution of the electrolytes (KCl, NaNO₃ etc.) instead of distilled water.
4. (a) Dry filter the solution; after rejecting the first few ml of the filtrate collect the residual filtrate in a clean dry beaker. Pipette out 25 ml of this filtrate and titrate against the standardized NaOH solution using phenolphthalein indicator. Repeat the titration and record the concordant titre value.
(b) Perform the step 4(a) for the remaining two mixtures.
5. Calculate the solubility and solubility product accordingly.

Experiment No 4 : Determination of partition coefficient of Iodine or Acetic acid between water and an immiscible organic solvent.

Theory :

According to *Nernst distribution law*, if to a system consisting of two immiscible or slightly miscible liquids is added a third substance, which is soluble in both the liquids, the substance distributes itself between the two liquids in such a manner that the ratio of its molar concentrations (precisely, the activities) in the two liquids remains constant at a particular temperature.

The following equilibrium is established when iodine (I₂) is added to water in presence of an immiscible organic solvent :



Thus if $(a_{I_2})_w$ and $(a_{I_2})_o$ be the activities of the solute (I₂) in the two liquids, water (w) and organic solvent (o) at equilibrium, then,

$$K_d = \frac{(a_{I_2})_o}{(a_{I_2})_w} = \text{constant} \quad (2)$$

The constant, K_d is the *distribution coefficient*, or, the *partition coefficient* of the solute (I₂) between the two liquids, organic solvent and water. This expression holds good so long as the solute retains the same state of aggregation in the two solvents, i.e., there is neither association nor dissociation of the solute in the two solvents and there occurs no chemical reaction between the solute and the solvents or even between the solvents.

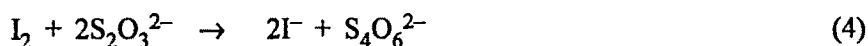
If both the phases are dilute solutions, then, the activity coefficients are very close to unity and molar concentration of the solute (I₂) in the two phases, $[I_2]_w$ and $[I_2]_o$, approach their activities respectively. So, distribution coefficient, K_d is then given by,

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$$K_d = \frac{[I_2]_o}{[I_2]_w} \quad (3)$$

Thus, by determining the concentrations of I_2 in the two liquid layers by titrating with a reducing agent, eg., sodium thiosulfate using starch indicator it is possible to determine the value of K_d at room temperature.

Thiosulfate ($S_2O_3^{2-}$) is oxidized by I_2 to tetrathionate ($S_4O_6^{2-}$) according to,



If V_1 ml of the aqueous layer of iodine requires for titration T_1 ml of S (N) thiosulfate solution, and V_2 ml of organic layer of iodine requires T_2 ml of $xS(N)$ thiosulfate solution ($x > 1$), then the partition coefficient, K_d will be

$$K_d = \frac{T_2 x S / V_2}{T_1 S / V_1} = x \left(\frac{T_2}{T_1} \right) \left(\frac{V_1}{V_2} \right) \quad (5)$$

Procedure :

1. Prepare 500 ml ($\sim N/20$) sodium thiosulfate solution. Prepare 250 ml of a ($N/100$) thiosulfate solution by exact dilution of 50 ml of the ($N/20$) solution in a 250 ml volumetric flask.
2. Prepare the following two sets in two clean 250 ml stoppered glass bottles.

Set	Water (ml)	Solution of Iodine in CCl_4 or $CHCl_3$ ($\sim 4\%$ w/v)	Pure Solvent (ml)
I	~ 100	~ 30	0
II	~ 100	~ 15	~ 15
3. Shake the bottles thoroughly for about 45 minutes and allow to settle till a clear separation of phases occurs.
4. For both sets take 25 ml aliquot for aqueous layer and 5 ml aliquot for organic layer. In case of titration of the organic layer add ~ 40 ml of distilled water, shake well and then titrate.
5. Titrate the organic layer with the ($N/20$) sodium thiosulfate solution and titrate the aqueous layer using the ($N/100$) thiosulfate solution. Use freshly prepared cold starch solution as indicator. Colour change at the end point will be from intense blue to colourless.

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Note :

- (1) Use a mechanical sucking pipette for transferring the organic layer.
- (2) The constancy of K_d follows from the thermodynamic principle that when two phases of the same substance are in equilibrium at constant temperature and pressure the chemical potential of the dissolved substance will be the same in both phases.
- (3) In case of distribution of acetic acid between water and an immiscible organic solvent determine the concentrations of acetic acid in both the phases by titration against a standard alkali.

Experiment No 5 : Determination of the rate constant for the first order acid catalyzed hydrolysis of an ester.

Theory :

Rate of first order reaction is directly proportional to the first power of the concentration of the reactant. A first order reaction may be represented as,



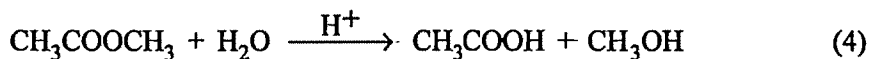
for which the rate,

$$-\frac{dC_A}{dt} = kC_A \quad (2)$$

where k is the rate constant (unit: time^{-1}) and C_A is the molar concentration of A at time t . Integration of the rate equation with proper limits at $t = 0$, $C_A = C_0$ and at $t = t$, $C_A = C_t$, converting the logarithmic term to base 10 (i.e., \log_{10}) one obtains,

$$k = \frac{2.303}{t} \log_{10} \frac{C_0}{C_t} \quad (3)$$

Hydrolysis of an ester (e.g. methyl acetate) although appearing to be bimolecular is kinetically a first order reaction with respect to the ester, since, water is present in large excess. The rate of the reaction also depends on the concentration of H^+ ion but H^+ being a catalyst is not consumed in the reaction and consequently its concentration remains constant in a given set.



The reaction is slow but is efficiently catalyzed by strong acids (say HCl ; H^+ is the active ion). When a known amount of an ester (methyl acetate) is allowed to hydrolyse in presence of a known amount of strong acid (say, HCl), the progress of the reaction may be studied by withdrawing measured volumes of aliquots from the reaction mixture at different intervals of time and titrating the same with an alkali solution using phenolphthalein as indicator. The volume of alkali required for a known volume of aliquot at any instant of time is equivalent

to the sum of the amount of acetic acid (a weak acid) formed and the amount of strong acid used as the catalyst (a fixed amount). If V_0 , V_1 and V_∞ be the volumes of the alkali required for the same volume of the aliquots—at the beginning, ($t = 0$), at time t and at the end of the reaction (infinite time, $t = \infty$), then,

$$(V_\infty - V_0) \propto C_0 \text{ initial concentration of the ester} \quad (5)$$

$$(V_t - V_0) \propto \text{concentration of ester consumed} = \text{concentration of weak acid formed}$$

$$\therefore \text{concentration of ester left} \propto [(V_\infty - V_0) - (V_t - V_0)] \propto (V_\infty - V_t) \propto C_t$$

Substituting in eqn (3)

$$\therefore k = \frac{2.303}{t} \log_{10} \left(\frac{V_\infty - V_0}{V_\infty - V_t} \right)$$

$$\therefore \log_{10} \left(\frac{V_\infty - V_0}{V_\infty - V_t} \right) = \left(\frac{k}{2.303} \right) t \quad (6)$$

Consequently since it is not possible to determine V_0 for the reaction, the first volume of NaOH, i.e V_1 will replace V_0 , consequently t will be replaced by Δt , where, $\Delta t = t_n - t_1$, $n = 2, 3, 4$, etc.

Thus, measuring V_1 , V_t and V_∞ and plotting $\log_{10} [(V_\infty - V_1) / (V_\infty - V_t)]$ against Δt , it is possible to determine k from the slope of the resulting straight line passing through the origin.

$$k = 2.303 \times \text{slope} \quad (7)$$

Procedure :

1. Prepare 250 ml of approximately 0.1 (N) NaOH solution, and 100 ml of ~1(N) HCl, or, 100 ml of ~0.5(N) HCl solutions.
2. Take 50 ml of the catalyst acid solution (HCl) in a 100 ml dry conical flask placed at the required temperature add 5 ml of the ester using a pipette and note the time of half discharge and mix uniformly.
3. Withdraw, using a pipette, 2 ml of an aliquot from the reaction mixture into 50 ml of ice-cold distilled water in a 250 ml conical flask. Note the time of half-discharge. Titrate against the 0.1 (N) NaOH solution using phenolphthalein as indicator. Take this titre as V_1 at time t_1 .
4. Repeat step 3 at different time intervals w.r.t. t_1 (3, 8, 15, 24, 35 minutes). Record the titre values (V_t) and time (t_n) in a tabular form.
5. After the required titrations are over, place the residual mixture on a hot water-bath and

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heat at $\sim 60^{\circ}\text{C}$ for ~ 30 minutes using an air-condenser. Cool to room temperature, take 2 ml of an aliquot into 50 ml of water and titrate against the same 0.1 (N) NaOH solution, using phenolphthalein as indicator as before. This titre value gives V_{∞} .

6. Plot $\log_{10} [(V_{\infty} - V_1) / (V_{\infty} - V_2)]$ vs. Δt and draw the best fit straight line passing through the origin and find k from the slope.

Note : V_{∞} may also be theoretically calculated.

Calculation of V_{∞}

- (1) Catalyst concentration is determined using (N/10) NaOH solution. (Standardized against oxalic acid solution)

- (2) Estimation of acid available from ester:

$$\text{Density} = 0.93 \text{ g.cm}^{-3}$$

So, 1 ml contains 0.93 g of ester

Hence, 5 ml (taken from the mixture) contain 0.93×5 g of ester = 0.0628 mol of ester (using methyl acetate)

- (3) Catalyst acid (HCl) strength = x mol/L [say 1.2 (N)]

So, 50 ml of catalyst acid (taken from the mixture) = $(x/1000) 50 = \{(1.2 \times 50) / 1000\}$ mol = 0.06 mol

Now the mixture of 50 ml acid catalyst + 5 ml ester contains (available acid) = $(0.06 + 0.0628)$ moles of total acid

\therefore 55 ml mixture contains 0.1228 mol of total acid

hence 2 ml (aliquot for each time) should contain available total acid = $\{(0.1228 \times 2) / 55\}$ mol = 4.465×10^{-3} mol acid

- (4) Strength of NaOH solution taken (say) = 1.05(N/10)

so, 0.105 moles of NaOH is in 1000 ml alkali solution

so, 4.465×10^{-3} mol of NaOH is in 42.52 ml [4.465×10^{-3} moles of acid $\equiv 4.465 \times 10^{-3}$ moles of alkali]

so, $V_{\infty} = 42.52$ ml

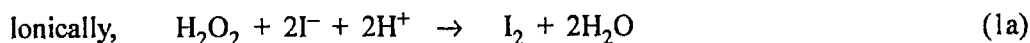
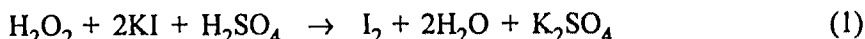
Hence, the general equation is

$$V_{\infty} = (4.465 / \text{strength of alkali in normality})$$

Experiment No 6 : Determination of rate constant of the reaction between H_2O_2 and acidified KI solution using clock reaction.

Theory :

In dilute acid medium (dil. H_2SO_4) H_2O_2 reacts with KI according to



$$t = 0 \quad a \quad 0$$

$$t = t \quad (a-x) \quad x$$

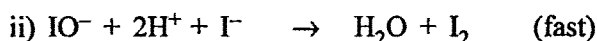
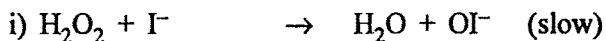
The overall reaction is kinetically of second order, being first order in H_2O_2 and first order in I^- .

The rate of the reaction may be expressed according to

$$\text{rate} = \frac{-d[\text{H}_2\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2][\text{I}^-] \quad (2)$$

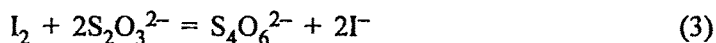
where, k is the second order rate constant, $[]$ represents molar concentration of the respective species. The unit of k is $\text{L mol}^{-1} \text{s}^{-1}$.

The reaction actually occurs in two steps:



The first step is the rate-determining step.

If the iodide ion concentration, $[\text{I}^-]$, is kept constant the reaction becomes kinetically first order in $[\text{H}_2\text{O}_2]$. This condition is achieved in two ways: (i) by adding sodium thiosulfate solution continuously in small amounts to the reaction mixture, when thiosulfate ($\text{S}_2\text{O}_3^{2-}$) ions react with the liberated I_2 and regenerate I^- according to



(ii) using a large excess of I^- ions in the system.

Under these conditions the rate equation (2) is transformed to

$$-d[\text{H}_2\text{O}_2]/dt = k_1[\text{H}_2\text{O}_2]$$

$$\text{where, } k_1 = k[\text{I}^-]$$

k_1 is the rate constant of the reaction. Integrating the above equation with the boundary conditions at $t = 0$, $[\text{H}_2\text{O}_2] = a$; at $t = t$, $[\text{H}_2\text{O}_2] = (a-x)$, where, x =amount of H_2O_2 reacted \equiv equivalent of I_2 liberated \equiv equivalent of thiosulfate consumed, one obtains

$$k_1 = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right) \quad (4)$$

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If, V_0 = titre value of thiosulfate for iodine liberated by a fixed volume, (say 10 ml) of H_2O_2 solution, this is equivalent to the initial concentration of H_2O_2 i.e., a .

V_t = titre value of the same thiosulfate solution for the iodine liberated by the same volume (10 ml) of H_2O_2 present in the reaction mixture (undergoing reaction) at time t ; this is equivalent to x .

Substituting for a and $(a-x)$ in the rate equation (4) one obtains the working equation,

$$k_1 = \frac{2.303}{t} \log \frac{V_0}{V_0 - V_t} \quad (5)$$

$$\log \frac{V_0}{V_0 - V_t} = \frac{k_1}{2.303} t \quad (6)$$

A plot of $\log [V_0 / (V_0 - V_t)]$ against t will be a straight line passing through the origin. k_1 may be evaluated from the slope.

Procedure :

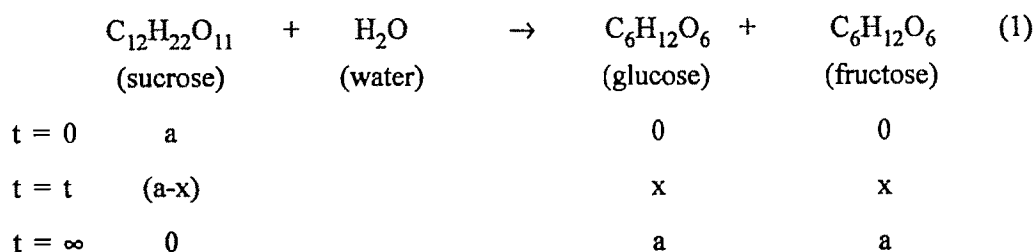
1. Prepare the following solutions.
 - i) 50 ml of "1-vol." H_2O_2 solution.
 - ii) 250 ml of KI solution (4 g of KI / litre)
 - iii) 50 ml of (1:2) H_2SO_4 solution (~12N),
 - iv) 250 ml of (~N/20) sodium thiosulfate solution :
2. Take 10 ml ~12 (N) H_2SO_4 , add 10 ml of 1-vol H_2O_2 using a pipette then add 2 g of solid KI. Cover the mouth of the 250 ml conical flask by a watch glass, keep the reaction mixture in the dark for 10 minutes. Add 150 ml of water to the flask and titrate the liberated iodine with (~N/20) thiosulfate solution using starch indicator. This titre value is V_0 .
3. Take 250 ml of the prepared (4g lit⁻¹) KI solution in a 500 ml conical flask, add 15 ml of ~12(N) H_2SO_4 solution and 5 ml of starch indicator. Fill the burette with the prepared thiosulfate solution. Add 10 ml of the 1-vol. H_2O_2 solution into the reaction mixture using a pipette and start the stop watch at the time of half discharge. Shake the reaction mixture. A blue colour will soon appear. Discharge the blue colour immediately by adding a small excess of the (~N/20) thiosulfate solution from a burette and note the burette reading. Record the time of reappearance of the blue colour. The volume of thiosulfate consumed will correspond to the time of reappearance of the blue colour. Continue this process and record at least 6 readings. These titre values give V_t .
4. Plot $\log[V_0 / (V_0 - V_t)]$ against time, t , and draw the best fit straight line passing through the origin. Calculate the value of the rate constant, k_1 , from the slope.

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Experiment No 1 : To study the kinetics of inversion of cane sugar using a polarimeter.

Theory :

Inversion of cane sugar (sucrose) takes place due to its hydrolysis in the presence of H^+ ions as catalyst in aqueous medium to produce glucose and fructose in equimolar proportion.



Since sucrose is *dextro-rotatory* (specific rotation $+66.5$) whereas the hydrolysed mixture consisting of equimolar quantities of glucose and fructose is *laevo-rotatory* (specific rotations $+52.7$ and -92.0 respectively at $25^\circ C$), an inversion in the sign of optical rotation of the solution occurs due to this reaction, which signifies the term *inversion*.

The rate of the reaction (1) depends upon the concentrations of sucrose, water and hydrogen ions. Water being present in large excess, its concentration remains virtually unchanged. Concentration of the H^+ ion also remains unchanged since it is not used up in the reaction. So, the rate of the reaction (1) is proportional to concentration of sucrose only. Thus the 'inversion' reaction (1) becomes kinetically of the *first order*.

The rate law of the reaction may be expressed according to (2) :

$$\text{rate} = -\frac{d}{dt} [\text{sucrose}] = \frac{d}{dt} [\text{glucose}] = \frac{d}{dt} [\text{fructose}] = k [\text{sucrose}] \quad (2)$$

where $[]$ represents concentration in mol L^{-1} , k is the first order rate constant.

If a is the initial concentration of sucrose at time, $t=0$ and x is the concentration of sucrose decomposed during time $t = t$, then $(a-x)$ is the concentration of sucrose remaining at time $t = t$. The rate equation (2) may be expressed as:

$$-\frac{d}{dt}(a-x) = k(a-x) \quad (3a)$$

or,

$$\frac{dx}{dt} = k(a-x) \quad (3b)$$

On integrating one obtains

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$$\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303} \quad (4)$$

If the quantities, x_1, x_2, \dots, x_n etc., or $(a-x_1), (a-x_2), \dots, (a-x_n)$ etc., are determined at different intervals of time respectively, then on rearranging equation (4) one obtains

$$\log\left(\frac{a-x_1}{a-x_n}\right) = \frac{k}{2.303}(t_n - t_1) \quad (5)$$

where, t_n and x_n represent the corresponding data of n -th recording, ($n > 1$). This formulation eliminates the need for accurate determination of the initial concentration a . The optical rotation (θ) is proportional to concentration of the optically active substance. If θ_0 and θ_∞ are the corrected angles of rotation at the beginning ($t = 0$) and at the end ($t = \infty$) of the reaction, and θ_1 and θ_n be the values at times t_1 and t_n , then $(\theta_0 - \theta_\infty)$ will be proportional to the initial concentration a , $(\theta_1 - \theta_\infty)$ will be proportional to $(a - x_1)$ and $(\theta_n - \theta_\infty)$ will be proportional to $(a - x_n)$ respectively. The relation (5) is thus transformed to (5a) :

$$k = \frac{2.303}{t_n - t_1} \log\left(\frac{\theta_1 - \theta_\infty}{\theta_n - \theta_\infty}\right) \quad (5a)$$

Thus, k can be determined from the slope of straight line obtained by plotting logarithmic terms of eqn. 5(a) against time interval $(t_n - t_1)$.

Since the strong acid (the catalyst) is completely dissociated at the concentration employed, the rate constants (k_I and k_{II}) of the reaction with two sets of concentrations of the strong acid are directly proportional to their concentrations $[\text{acid}]_I$ and $[\text{acid}]_{II}$.

$$\frac{k_I}{k_{II}} = \frac{[\text{acid}]_I}{[\text{acid}]_{II}} \quad (6)$$

It is assumed that the rate of reaction in pure water (only) is negligible.

Eq (6) indicates that the reaction is first order with respect to the catalyst (H^+ ion), which implies that H^+ ion is a homogeneous catalyst for this reaction.

Procedure :

1. Prepare 25% (w/v) solution of cane sugar by weighing ~25 g. of the sugar and dissolving the same in 100 ml of water in a 250 ml beaker.
2. Prepare 100 ml of ~2(N) HCl solution and 50 ml of ~(N) HCl solution by exact dilution of the ~12(N) HCl solution.

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3. Pipette out 25 ml of the sugar solution in a dry conical flask. To it add 25 ml of the $\sim(2N)$ HCl solution using a pipette and start the stopwatch at the time of half-discharge.
4. Fill the polarimeter tube with the reaction mixture, place the tube in the polarimeter, record the angle of rotation and the time.
5. Measure the angle of rotation at increasing time intervals record the (θ_n, t_n) data. Take at least six readings.
6. Wash the polarimeter tube with distilled water and repeat the steps 3 to 5 with the (N) HCl solution.
7. For the determination of the angles of rotation (θ_∞) at infinite time, heat the remaining parts of the two reaction mixtures separately at $\sim 60^\circ\text{C}$ in a water bath for about 45 minutes, cool to room temperature and measure the angles of rotation as before.
8. Plot

$$\log\left(\frac{\theta_1 - \theta_\infty}{\theta_n - \theta_\infty}\right) \text{ vs } (t_n - t_1)$$

and find the rate constants (k_I and k_{II}). Hence find k_I/k_{II} and interpret the result.

9. Record the room temperature.

Experiment No 2 : To study the phase diagram of a binary system (phenol-water) and the effect of impurities (eg. NaCl).

Theory :

A diagram representing the conditions of equilibrium among different forms or phases of a substance or of a mixture of substances is called a phase diagram. When the position of such an equilibrium is influenced only by such variables as temperature, pressure and concentration, but not by such factors as gravity, surface tension, electrical and magnetic forces, the number of degrees of freedom (F) of the system may be related to the number of components (C) and the number of phases (P) according to the *phase rule* equation: $F = C - P + 2$.

In a binary mixture of two partially miscible liquids e.g., phenol and water, two phases are formed. When water is gradually added to phenol, water passes into solution until a saturated solution of water in phenol is obtained. A new phase of different density, consisting of a saturated solution of phenol in water appears on addition of further quantities of water. Increase in the concentration of water increases the volume of the second phase (i.e., phenol in water) and decreases the volume of the first phase (i.e., water in phenol), but the relative concentrations of the components in either phase remain constant. Such mutually saturated liquid pairs in contact with each other constitutes a *univariant system*, the only variable being the temperature,

the pressure being kept constant. Rise of temperature brings about a change in the mutual solubilities of the two liquids. The solubility curve of phenol water system (Fig. 1) shows that the mutual solubilities increase with increase of temperature. The two phases have a unique composition called *consolute composition* at a certain temperature (t_c) called *critical solution temperature (CST)*, or, *consolute temperature (CT)*. For phenol water system $t_c = 65.9^\circ\text{C}$ is the *upper critical solution temperature (UCST)* and the consolute composition is, water 66% and phenol 34%. Above this temperature the two liquids are completely miscible. The liquid pair indicated by any point (x) in between the two solubility curves will separate into two phases indicated by two points A and A', while any liquid pair represented by any point outside the curve will form a single phase. Lines (such as A A') joining the two mutual solubilities at any given temperature are called *tie-lines* and the two solutions represented by the compositions A and A' are called *conjugate solutions*. As pressure is fixed throughout the experiment, $F = C - P + 1 = 2 - 1 + 1 = 2$. That is, such a system will be bivariant at any point outside the curve. So only two degrees of freedom, i.e., temperature and composition, should be specified in order to define the system completely. In region under the solubility curve there are two phases, i.e., $P = 2$, $C = 2$ (as before), hence, $F = C - P + 1 = 2 - 2 + 1 = 1$. That is, such systems will be univariant, the temperature alone will define the system completely. Therefore, the two phases at any given temperature will have definite compositions, irrespective of their amounts.

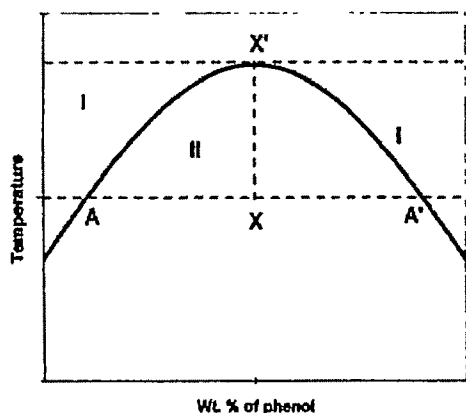


Fig. 1. Solubility curve of phenol-water system

When a third substance, such as, NaCl is added to a binary mixture of two partially miscible liquids (e.g., phenol-water) the mutual solubility of the liquids will depend upon the chemical nature and quantity of the third substance. Mutual solubilities generally decrease when the third substance is soluble only in one of the two liquids, and consequently consolute temperature rises. When the third substance dissolves in both the liquids consolute temperature is generally lowered.

At any point on the solubility curves, say at A or A', $C = 2$ and $P = 2$, one of two conjugate solutions has a mere existence. Hence, $F = C - P + 1 = 2 - 2 + 1 = 1$, i.e., solubility has a definite value at a particular temperature.

At the point x' on this curve, the two conjugate solution have identical composition, $C = 2 - 1 = 1$, $P = 2$; hence, $F = C - P + 1 = 1 - 2 + 1 = 0$. Therefore, the system represented by this point x' is *invariant*, since temperature (t_c) and composition are automatically fixed.

If we calculate mean values of the compositions of the two conjugate solutions at several temperatures, and plot these points against corresponding temperatures, a straight line will always be obtained, which passes through the critical composition at the critical temperature. This “law of rectilinear diameter” as applied to partially miscible liquid pairs is obviously an extension of the corresponding law of Cailletet and Mathias on critical phenomena in the liquid-gas equilibrium.

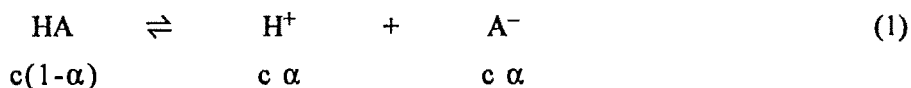
Procedure :

1. Weigh out accurately about 4 g of phenol (**caution: corrosive**) from a weighing bottle into a hard glass test tube.
2. Add 2 ml of water (or NaCl solution) to it from a burette. Clamp the test tube inside a large beaker fitted with a glass stirrer. Insert a thermometer into the test tube. Pour sufficient amount of water in the beaker.
3. Heat the water in the beaker uniformly, while stirring it all the time. The mixture in the test tube which was initially turbid, becomes suddenly clear at a particular temperature. Note the temperature. Allow the whole system to cool. Record the temperature at which turbidity reappears. Take the mean of these two temperatures (disappearance and reappearance).
4. Go on adding 1 ml portions of water (or NaCl solution) and at each step note the temperature for disappearance and reappearance of turbidity. When the mean temperature starts decreasing add 2ml/3 ml of water/NaCl solution each time and note the mean temperature. Continue the addition till the mean temperature drops to nearly 55°C.
5. Find the weight percentages of phenol in the mixture from the known weights of phenol and water (density of water or NaCl solution ~1 g/ml).
6. Draw the solubility curve by plotting the mean temperature against weight percentage of phenol. Determine the upper critical solution temperature and the consolute composition for the system. Interpret your result.

Experiment No 3 : To determine the ionisation constant of a weak acid by conductometric method.

Theory :

A monobasic weak acid HA, is partially ionised in aqueous solution.



The ions are aquated and the degree of ionisation (α) increases with dilution.

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The degree of ionisation at a particular concentration (c) of the weak electrolyte HA may be well approximated by the ratio Λ/Λ_0 where, Λ is the equivalent conductance of HA at concentration c and Λ_0 is its equivalent conductance at infinite dilution. Ionisation constant (K_a) of the weak acid, HA, may be defined as

$$K_a = \frac{a_{H^+} a_{A^-}}{a_{HA}} \quad (2)$$

where a stands for the activity of the respective species. Since $a = \text{molar concentration} \times f$, where f is the ionic activity coefficient, Eq. (2) may be transformed to

$$K_a = \frac{[H^+][A^-]}{[HA]} \cdot \frac{f_{H^+} f_{A^-}}{f_{HA}} \quad (3)$$

For a dilute solution of weak acid the ionic strength of the medium will be very low and the numerical values of the activity coefficients f are very close to unity (*Debye-Hückel limiting law*). Under this condition Eq. (3) may be written as

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (3a)$$

$$= c\alpha^2/(1 - \alpha) \quad (3b)$$

Substituting, one obtains from Eq. (3b)

$$K_a = \frac{c(\Lambda/\Lambda_0)^2}{1 - \Lambda/\Lambda_0} \quad (4)$$

which on rearrangement yields,

$$1/\Lambda = 1/\Lambda_0 + \Lambda c/(K_a \Lambda_0^2) \quad (5)$$

If a series of solutions of the weak acid (HA) of different concentrations are prepared and their equivalent conductances are determined by measuring their conductances in a cell of known cell constant, then by plotting $1/\Lambda$ against Λc , one may obtain a straight line with a positive intercept $1/\Lambda_0$ of and a positive slope of $(1/K_a \Lambda_0^2)$. Thus, K_a may be calculated using the relation :

$$K_a = (\text{intercept})^2/(\text{slope}) \quad (6)$$

provided Λ_0 is determined with sufficient accuracy. Therefore, by this method, the ionisation constant (K_a) as well as the equivalent conductance at infinite dilution (Λ_0) of a weak electrolyte (HA) can be determined.

Procedure:

1. Prepare 250 ml of a standard KCl solution (strength slightly higher than N/10) in *conductivity water*. Prepare 100 ml of an exact (N/10) KCl solution by quantitative dilution of the standard stock solution and 100 ml of an exact (N/100) KCl solution by accurately diluting the prepared standard (N/10) KCl solution with conductivity water.
2. Rinse a 100 ml beaker and the conductivity cell with the exact (N/100) KCl solution thoroughly and then pour sufficient volume of this solution into the beaker so that the electrodes of the cell are completely immersed in the solution. Record the conductance. Repeat this procedure with the exact (N/10) KCl solution. Calculate the *mean cell constant* from the measured conductance values of these two solutions, using the literature values of the specific conductance of KCl solutions at these concentrations at the same temperature.
3. Prepare 100 ml (~N/10) oxalic acid solution by accurate weighing of the solid oxalic acid. Prepare (~N/10) NaOH and standardize the same with the prepared oxalic acid, using phenolphthalein as the indicator. Prepare (~N/10) acetic acid solution and standardize the same against the standardized NaOH solution.
4. Prepare 100 ml of an exact (N/50) acetic acid solution by accurate dilution of the (N/10) solution with conductivity water using a volumetric flask.
5. Measure the conductance of the conductivity water used for this experiment. Subtract the value of this conductance from the recorded conductances of all solutions to obtain the corrected values.
6. In a clean dry 100 ml beaker take 50 ml of the (N/50) acetic acid solution using a 25 ml pipette. Dip the clean dry conductivity cell into this solution, stir well and record the conductance. Carefully pipette out 25 ml of (N/50) acetic acid solution and pour in exactly 25 ml conductivity water into the cell using the same pipette after washing it properly. Mix the solution well and record the conductance of this (N/100) acetic acid solution as before. Follow the same procedure of progressive dilution to obtain (N/200), (N/400) and (N/800) acetic acid solutions and record their conductances. Apply corrections for the conductance of the water used.
7. Calculate the equivalent conductance values of all the acetic acid solutions using the mean value of the cell constant with the aid of the relation $\Lambda = 1000\kappa/c$, where κ denotes the specific conductance.
8. Plot $(1/\Lambda)$ versus Λc and find Λ_0 from the intercept. Estimate K_a from the slope and intercept using equation (6).

Note : Compare the experimental value of Λ_0 obtained from the intercept with the calculated value of Λ_0 of acetic acid using the known ion conductance values for hydrogen ion and acetate

ion with proper temperature correction. [$\lambda_{\text{H}^+}^0 = 349.82$ and $\lambda_{\text{CH}_3\text{COO}^-}^0 = 40.9 \text{ ohm}^{-1}\text{cm}^2 \text{ g.equivalent}^{-1}$ at 25°C .]

$$\lambda_t = \lambda_{25} [1 + \alpha (t - 25)], \text{ t is temperature in degree C,}$$

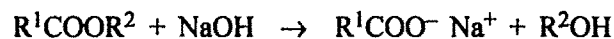
$$\alpha = 0.0142 \text{ for } \text{H}^+ ; = 0.016 \text{ for } \text{OH}^- ; = 0.02 \text{ for other anions.}$$

Utilize the theoretical value of Λ_0 to calculate K_a and compare with that obtained graphically.

Experiment No 4: To study the kinetics of saponification of ester by conductometric method.

Theory :

When an ester (R^1COOR^2) derived from a monocarboxylic acid (R^1COOH) and a monohydric alcohol (R^2OH) is treated with a caustic alkali (NaOH), the ester is hydrolysed to produce the alcohol and sodium salt of the acid :

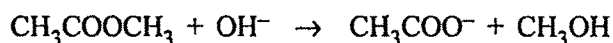


or,



Such alkaline hydrolysis of an ester is called *saponification*.

Methyl acetate ($\text{CH}_3\text{COOCH}_3$) on alkaline hydrolysis produces methanol (CH_3OH) and acetate (CH_3COO^-) :



$t = 0$	a	a	0	0
$t = t$	$a-x$	$a-x$	x	x
$t = \infty$	0	0	a	a

The overall reaction is kinetically of second order, being first order with respect to each of the reactants, the ester and hydroxyl ions (OH^-). The rate of the overall reaction may be expressed as

$$\text{rate} = -d[\text{ester}]/dt = k[\text{ester}] [\text{OH}^-] \quad (1)$$

where k is the rate constant and $[]$ stands for concentration in molarity. If the initial concentrations of both ester and alkali be a and those after time t be $(a-x)$ where, x is the amount of alkali/ester consumed, then,

$$\frac{dx}{dt} = k \cdot (a-x)^2 \quad (2)$$

Integration of equation (2), for $x = 0$, when, $t = 0$ yields.

$$k = \frac{1}{at} \cdot \frac{x}{a-x} \quad (3)$$

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The progress of the reaction can be monitored by measuring the electrolytic conductance of the reaction mixture, since the highly conducting OH^- ions ($\lambda_0 = 198.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eqv}^{-1}$) are replaced by weakly conducting CH_3COO^- ions ($\lambda_0 = 40.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eqv}^{-1}$). If C_0 , C_t and C_∞ be the conductances of the reaction mixture at the times $t = 0$, t , and at the completion of the reaction (infinite time, $t = \infty$), then,

$$a \propto (C_0 - C_\infty) \quad 4(a)$$

$$x \propto (C_0 - C_t) \quad 4(b)$$

$$(a-x) \propto (C_t - C_\infty) \quad 4(c)$$

Equation (3) is then transformed to:

$$\frac{(C_0 - C_t)}{(C_t - C_\infty)} = ka \cdot t \quad (5)$$

A plot of $[(C_0 - C_t) / (C_t - C_\infty)]$ versus t will be a straight line passing through the origin with a positive slope $= ka$. Thus, k may be evaluated from the relation,

$$k = \text{slope}/a. \quad (6)$$

Procedure :

1. Prepare 100 ml of standard ($\sim N/10$) oxalic acid solution by accurate weighing.
2. Prepare 250 ml of ($\sim N/10$) NaOH solution and standardize the same against standard ($N/10$) oxalic acid using phenolphthalein indicator. Prepare 100 ml of exact ($N/60$) NaOH solution by accurate dilution of the standardized NaOH solution in a 100 ml volumetric flask.
3. Prepare 250 ml of ($\sim N/10$) acetic acid and standardize the same against the standardized NaOH solution using phenolphthalein indicator. Prepare 100 ml of exact ($N/60$) acetic acid solution by accurate dilution of the standardized acetic acid solution in a 100 ml volumetric flask.
4. Pipette out 25 ml ($N/60$) NaOH solution in a clean dry 100 ml beaker, add 25 ml conductivity water using the same pipette. Mix thoroughly and measure its conductance (C_0).
5. Prepare an exact ($N/120$) solution of sodium acetate, $\text{CH}_3\text{COO}^-\text{Na}^+$, by mixing equal volumes of ($N/60$) CH_3COOH and ($N/60$) NaOH solutions. Measure the conductance of this solution (C_∞).
6. Note the density of the ester (methyl acetate) at room temperature. Prepare a standard solution of the ester by taking 1 ml of it (in a graduated pipette) and diluting it to 100 ml with water in a 100 ml volumetric flask. Calculate the strength of the solution ($\text{MW} = 74$). From this stock solution prepare, by accurate dilution, 100 ml of exactly ($N/60$) solution.

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7. In a clean dry 100 ml beaker, take 25 ml of (N/60) methyl acetate, and add 25 ml of (N/60) NaOH to it from a pipette and note the time of half-discharge. Measure the conductance (C_t) of the reaction mixture at different times (1, 2, 3 minutes, etc) Take 10 such readings. Record the conductance vs. time data in a tabular form. Record the temperature of the experiment.
8. Plot $(C_0 - C_t) / (C_t - C_\infty)$ against t to obtain rate constant, k , from the slope and the initial concentration, a ($= N/120$) of the ester. For this experiment normality = molarity for each of the solutions.

Experiment No. 5 : To determine the equilibrium constant of the reaction $KI + I_2 \rightleftharpoons KI_3$ by partition method.

Theory:

In aqueous solution iodine (I_2) reacts with potassium iodide (KI) to produce potassium tri-iodide (KI_3) according to:



for which the equilibrium constant K is given by

$$K = \frac{(a_{I_3^-})_w}{(a_{I^-})_w (a_{I_2})_w} \quad (1a)$$

where, a represents the activity of the species at equilibrium, and the subscript 'w' stands for aqueous solution. For dilute solution, the activities (a) are very close to molar concentrations (since the activity coefficients approach unity) and the equilibrium constant, K , may be expressed in terms of molar concentrations (C) according to:

$$K = \frac{(C_{I_3^-})_w}{(C_{I^-})_w (C_{I_2})_w} \quad (1b)$$

The equilibrium concentration of I_2 in aqueous solution, $[I_2]_w$, may be obtained from the partition coefficient by the application of Nernst distribution law, which states that when a solute is in contact with two immiscible solvents, the solute distributes itself between the two solvents in such a way that at equilibrium the ratio of the activities (i.e., molar concentrations, for dilute solutions) of the solute in the two solvents is a constant, at a particular temperature, called the partition coefficient or the distribution coefficient (K_d). Thus, when the solute iodine is in equilibrium with water (w) and an immiscible organic solvent (o), the partition coefficient, K_d , may be expressed as

$$K_d = (C_{I_2})_o / (C_{I_2})_w \quad (2)$$

$$\text{So, } (C_{I_2})_w = (C_{I_2})_o / K_d$$

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If C = total concentration of KI (i.e., I^-) initially present

C_w = total concentration of iodine (i.e., free $I_2 + I_3^-$) in aqueous layer at equilibrium, then,

$$(C_{I_3^-})_w = C_w - (C_{I_2})_w = C_w - \frac{(C_{I_2})_o}{K_d}$$

$$C = (C_{I^-})_w + (C_{I_3^-})_w \quad (3)$$

$$\therefore (C_{I^-})_w = C - (C_{I_3^-})_w = C - \left[\frac{(C_{I_2})_o}{K_d} \right] \quad (4)$$

Thus, the working expression for the equilibrium constant, K , becomes,

$$K = \frac{\left[C_w - \frac{(C_{I_2})_o}{K_d} \right]}{\left[C - \left\{ C_w - \frac{(C_{I_2})_o}{K_d} \right\} \right] \left[\frac{(C_{I_2})_o}{K_d} \right]} \quad (5)$$

Procedure :

1. Prepare 250 ml of standard (N/20) $K_2Cr_2O_7$ solution and 250 ml of standard (N/20) KI solution by accurate weighing.
2. Prepare 500 ml (~N/20) sodium thiosulfate solution and standardise the same against the standard (N/20) $K_2Cr_2O_7$ solution iodometrically using starch indicator following the usual procedure.
3. Prepare any two of the following four experimental sets of following compositions in 250 ml stoppered glass bottles :

Set	I	II	III	IV
Volume (ml) of KI solution	10	20	30	40
Volume (ml) of Iodine solution in organic solvent	~40	~40	~40	~40
Volume (ml) of Water	90	80	70	60

4. Stopper the glass bottles properly and shake the mixtures thoroughly for 45 minutes and allow to settle till a clear separation of the two phases occurs.
5. Record the room temperature.
6. For titration of I_2 in the organic layer take an aliquot of 10 ml add ~40 ml of water. Shake thoroughly and titrate with the standard (~N/20) thiosulfate solution using starch indicator. Estimate the concentration of iodine in organic layer.

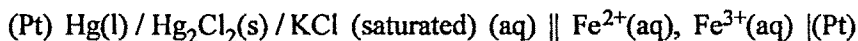
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- For titration of iodine in the aqueous layer, take an aliquot of 10 ml and ~40 ml of water and titrate with the standard (N/20) thiosulfate solution using starch indicator and find C_w , the total concentration of iodine in aqueous layer.
- Calculate the value of K at room temperature, using the value of the supplied partition coefficient, K_ϕ and interpret the results.

Experiment No. 6 : Determination of E° of Fe^{3+}/Fe^{2+} couple in the hydrogen scale by potentiometric titration of ferrous ammonium sulfate solution using $KMnO_4$, or, $K_2Cr_2O_7$ as standard.

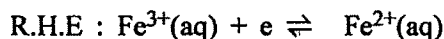
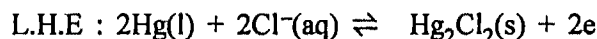
Theory :

When the Fe^{3+}/Fe^{2+} redox system is coupled with a saturated calomel electrode (SCE) as the reference electrode, the following electrochemical cell is produced:

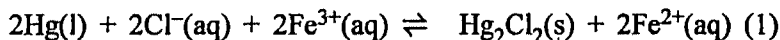


where the symbol \parallel stands for agar-KCl salt bridge which minimizes the liquid junction potential.

The half-cell reactions at the electrodes are :



Overall cell reaction is,

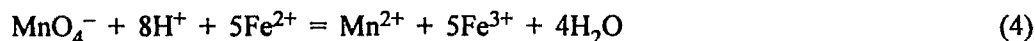
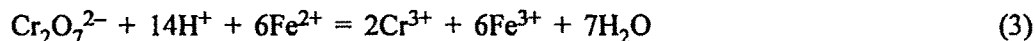


The e.m.f of the cell (E_{cell}) is given by,

$$E_{cell} = E_R - E_L$$

$$= E_{Fe^{3+}/Fe^{2+}}^0 + 0.059 \log \left\{ \frac{[Fe^{3+}]}{[Fe^{2+}]} \right\} - E_{SCE} \text{ (at } 25^\circ C) \quad (2)$$

Since E_{SCE} remains unchanged, if the temperature remains unchanged, the e.m.f of the cell (E_{cell}) varies with variation of the ratio, $[Fe^{3+}] / [Fe^{2+}]$. If an oxidant ($K_2Cr_2O_7$ or $KMnO_4$ as the case may be) is added to a solution of Fe^{2+} in acid medium, concentration of Fe^{2+} will fall and that of Fe^{3+} will rise due to the reactions :



With the addition of oxidant, the ratio ($[Fe^{3+}] / [Fe^{2+}]$) progressively increases, consequently E_{cell} increases. The standard reduction potential of an electrode may be defined as the emf of the cell produced by coupling standard hydrogen electrode on the left and the electrode under

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consideration on the right with all reactants and products at unit activities. Plot of E_{cell} versus volume(or number of drops)of the oxidant added is generated. The standard electrode potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ system can be determined from the graph as follows :

At the half equivalence point, exactly half of the Fe^{2+} originally present is converted to Fe^{3+} , and the ratio ($[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$) becomes unity. At this point,

$$E_{\text{cell}} = E_{1/2} = E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E_{\text{SCE}}$$

$$\therefore E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{1/2} + E_{\text{SCE}}$$

E_{SCE} is obtainable from literature. Thus, $E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ at room temperature may be obtained.

Note : Strictly speaking, this is the formal potential for the couple. This is due to the fact that $[\text{Fe}^{3+}] = [\text{Fe}^{2+}]$ does not necessarily imply $a_{\text{Fe}^{3+}} = a_{\text{Fe}^{2+}}$ because of the difference of the activity coefficients of the two ions.

Procedure :

- Prepare 100 ml of ($\sim N/2$) $\text{K}_2\text{Cr}_2\text{O}_7$ solution by accurate weighing using a digital balance.
 - Prepare 100 ml ($\sim N/2$) KMnO_4 solution, (a secondary standard).
 - Prepare 100 ml of ($\sim N/20$) solution of Mohr salt, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ in $\sim 2(N)$ H_2SO_4 .
- Take an aliquot of 10 ml of Mohr salt solution in a beaker and dip a clean Pt electrode into this solution. Add sufficient volume of $\sim 2(N)$ H_2SO_4 so that the electrode dips properly. Connect this half-cell with a saturated calomel electrode (SCE) through an agar-KCl salt bridge. Complete the connection of this experimental cell with the potentiometer.
- Standardize the potentiometer with a standard cell. Measure the volume of 1 drop of titrant.
- Measure the e.m.f (E_{cell}) of the experimental cell.
- Add 2-drops of ($N/2$) $\text{K}_2\text{Cr}_2\text{O}_7$ / ($N/2$) KMnO_4 solution, stir gently and record the E_{cell} . Repeat the procedure till 10 drops of titrant are added. Then add 1 drop at a time till the equivalence point is reached, which is indicated by a sharp increase of E_{cell} . Take a few more readings beyond the equivalence point.
- Plot, (a) E_{cell} versus number of drops (n) of $\text{K}_2\text{Cr}_2\text{O}_7$ (or KMnO_4) solution.
 (b) $|\Delta E_{\text{cell}} / \Delta n|$ versus n (number of drops). Find the equivalence point and hence the value of E_{cell} corresponding to the half-equivalence point (i.e., $E_{1/2}$). Calculate E° of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system using the literature value of E_{SCE} .

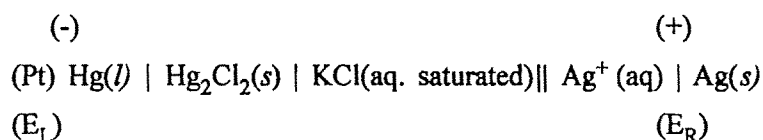
$$E_{\text{SCE}} \text{ at } t^{\circ}\text{C} = [0.2415 - 0.00076 (t-25)] \text{ volt.}$$

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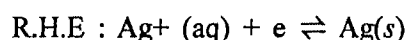
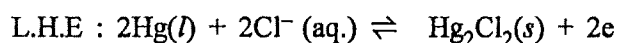
Experiment No. 7 : Determination of concentration of (i) AgNO_3 solution and (ii) solubility product of AgCl by potentiometric titration of AgNO_3 solution against standard KCl solution.

Theory :

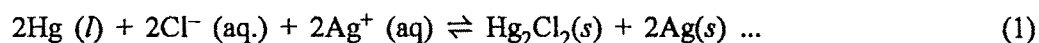
When the $\text{Ag}^+/\text{Ag}(s)$ redox electrode is coupled with a saturated calomel electrode (SCE) the following electrochemical cell is produced :



where, the symbol \parallel stands for agar- KNO_3 salt-bridge, which minimizes the liquid junction potential. The half cell reactions at the electrodes are:



The overall cell reaction is :



and the e.m.f. of the cell is given by :

$$\begin{aligned} E_{\text{cell}} &= E_R - E_L = E_{\text{Ag}^+/\text{Ag}} - E_{\text{SCE}} = \\ &E_{\text{Ag}^+/\text{Ag}}^0 + 0.059 \log \left[a_{\text{Ag}^+} / a_{\text{Ag}(s)} \right] \quad (\text{at } 25^\circ\text{C}) \quad 1(a) \end{aligned}$$

$\text{Ag}(s)$ being in the standard state, its activity will be unity. For a dilute solution activity (a) of Ag^+ ion may be replaced by the numerical value of its concentration $[\text{Ag}^+]$. Thus,

$$E_{\text{Cell}} = E_{\text{Ag}^+/\text{Ag}}^0 + 0.059 \log [\text{Ag}^+] - E_{\text{SCE}} \quad (\text{at } 25^\circ\text{C}) \quad 1(b)$$

Since $E_{\text{Ag}^+/\text{Ag}}^0$ and E_{SCE} are fixed, E_{cell} depends on $[\text{Ag}^+]$.

The standard reduction potential of an electrode may be defined as the emf of the cell produced by coupling standard hydrogen electrode on the left and the electrode under consideration on the right with all reactants and products at unit activities.

As KCl solution is added to AgNO_3 solution the following reaction takes place:



AgCl being sparingly soluble, $[\text{Ag}^+]$ decreases as more and more KCl solution is added, resulting in a decrease of E_{Cell} with increase in the number of drops (n) of KCl solution. Near the

equivalence point, addition of a small volume (1 drop) of KCl solution removes practically all the Ag^+ ions from the solution. This produces an abrupt decrease in E_{cell} and the $\Delta E_{\text{cell}}/\Delta n$ value is also very large. All the Ag^+ ions present in the solution at the equivalence point come from the dissociation of the sparingly soluble AgCl produced :



The activity solubility product, K_a of AgCl may be defined as:

$K_a = a_{\text{Ag}^+} a_{\text{Cl}^-}$, and is called the activity solubility product.

Now,

$$K_a = [\text{Ag}^+][\text{Cl}^-]f_{\text{Ag}^+}f_{\text{Cl}^-} \quad (4)$$

$$= K_{\text{sp}} \cdot f_{\pm}^2 \quad (5)$$

where, K_{sp} is called the concentration solubility product or simply solubility product, and f_{\pm} is the mean ionic activity coefficient.

For a dilute solution, the activities may be replaced by the numerical values of concentrations.

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

At equivalence point

$$[\text{Ag}^+] = [\text{Cl}^-],$$

So,

Substituting this value of $[\text{Ag}^+]$ in Eq. (1b), one obtains the e.m.f. of the cell at the equivalence point:

$$E_{\text{cell}}(\text{eqv.}) = E^0_{\text{Ag}^+/\text{Ag}} + 0.0295 \log K_{\text{sp}} - E_{\text{SCE}} \quad (6)$$

Thus, by determining E_{cell} at the equivalence point potentiometrically and knowing $E^0_{\text{Ag}^+/\text{Ag}}$ and E_{SCE} from literature, one may calculate K_{sp} using the relation

$$K_{\text{sp}} = \text{anti log} \{ [E_{\text{Cell}}(\text{eqv.}) + E_{\text{SCE}} - E^0_{\text{Ag}^+/\text{Ag}}] / 0.0295 \} \quad (7)$$

After the equivalence point the addition of more KCl solution will lower the concentration of Ag^+ further. The constancy of K_{sp} demands

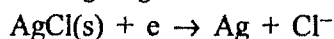
$$[\text{Ag}^+] = K_{\text{sp}} / [\text{Cl}^-] \quad (8)$$

Hence, E_{cell} will decrease with increase of $[\text{Cl}^-]$ according to,

$$\begin{aligned} E_{\text{cell}} &= E^0_{\text{Ag}^+/\text{Ag}} + 0.059 \log K_{\text{sp}} - 0.059 \log [\text{Cl}^-] - E_{\text{SCE}} \\ &= E^f_{\text{Ag}^+/\text{Ag}} - E_{\text{SCE}} - 0.059 \log [\text{Cl}^-] \end{aligned} \quad (9)$$

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where, $E_{\text{Ag}^+/\text{Ag}}^f$ represents the formal potential of



redox system and is given by

$$E_{\text{Ag}^+/\text{Ag}}^f = E_{\text{Ag}^+/\text{Ag}}^0 + 0.059 \log_{10} K_{\text{sp}} \quad (10)$$

From the plot of E_{cell} vs. volume or number of drops (n) of KCl solution it is possible to find the volume (V) or the number of drops (n) of KCl required to completely precipitate the Ag^+ ions present in the solution, and the value of E_{cell} at the equivalence point. The derivative plot, $|\Delta E_{\text{cell}} / \Delta n|$ vs. n shows a maximum at the value of n corresponding to the equivalence point. The strength of the AgNO_3 solution may now be calculated using the relation :

$$V(\text{AgNO}_3) \times S(\text{AgNO}_3) = V(\text{KCl}) \times S(\text{KCl})$$

Thus, from potentiometric titration the strength of AgNO_3 solution and also the value of solubility product of AgCl may be determined.

Note : One may carry out some geometrical constructions in the E vs n plot in order to fix the E_{cell} at the equivalence point exactly. Three procedures may be adopted for this purpose (i) the method of bisection (ii) the method of parallel tangents (iii) the method of circle fitting. [Reference : Vogel's Quantitative Chemical Analysis 5th edn.]

Procedure :

1. Prepare an agar- KNO_3 salt bridge. Record the room temperature.
2. Prepare 100 ml of (N/100) AgNO_3 solution in distilled water.
3. Prepare 100 ml of a standard (N/10) KCl solution in distilled water by accurate weighing, using a digital balance.
4. Take 10 ml of the prepared AgNO_3 solution in a 100 ml beaker and dip the silver electrode in this solution. Add sufficient amount of distilled water so that the electrode dips properly. This constitutes the experimental electrode $\text{Ag}^+/\text{Ag(s)}$.
5. Set up the experimental cell by connecting the saturated calomel electrode (SCE) and the experimental electrode through the agar- KNO_3 salt bridge.
6. Take the prepared KCl solution in a burette and determine the volume of 50 drops and then calculate the volume of 1 drop of KCl.
7. Connect the experimental cell with the standardized potentiometer.
8. Measure the e.m.f. of the cell (E_{cell}). Add 2-drops of (N/10) KCl solution, stir gently and record the E_{cell} . Repeat the procedure till 10 drops of titrant are added. Then add 1 drop at a time till the equivalence point is reached, which is indicated by a sharp decrease of E_{cell} . Take a few more readings beyond the equivalence point.

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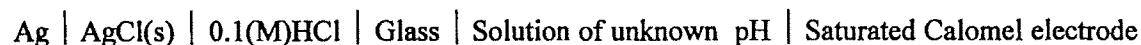
9. Plot (i) the observed E_{cell} values against number of drops of KCl solution added, (ii) $|\Delta E_{\text{cell}} / \Delta n|$ versus n . Determine the equivalence point and the E_{cell} value at the equivalence point from the graph. Calculate the solubility product of AgCl using the literature values of $E^0_{\text{Ag}^+/\text{Ag}}$ and E_{SCE} .
10. Calculate the strength of the AgNO_3 solution by using the volume of standard KCl solution required at equivalence point (obtained graphically).

Note : E_{SCE} at $t^\circ\text{C} = [0.2415 - 0.00076 (t-25)]$ volt. $E^0 (\text{Ag}^+/\text{Ag}(s)) = 0.799$ volt at 25°C . For experimental temperature (T) other than 298K substitute the factor $0.0295(T/298)$ for 0.0295 in Eq. 7.

Experiment No 8 : Determination of pK values of weak monobasic, dibasic and polybasic acids by pH-metric method.

Theory :

The pH of an aqueous solution can be measured using glass-calomel electrode system in which following electrochemical cell is formed:



The right hand electrode is the saturated calomel electrode (SCE) and the left hand electrode is the glass electrode which is actually an ion selective membrane electrode, reversible with respect to H^+ ion. The glass electrode is the most widely used hydrogen ion responsive electrode and its use depends on the fact that when a glass membrane is immersed in a solution, a potential is developed which is a linear function of the hydrogen ion concentration of the solution. The internal HCl solution is maintained at constant concentrations, the potential of the silver-silver chloride electrode inserted into it will be constant, and so too will the potential between HCl solution and the inner surface of the glass bulb. Hence the only potential which can vary is the potential between the outer surface of the glass bulb and the test solution in which it is immersed, so the overall potential of the electrode is governed by the hydrogen ion concentration of the test solution. Glass electrodes are also available as combination electrode which contain the indicator electrode and a reference electrode combined in a single unit. The potential (E_g) of the glass electrode at 25°C may be expressed as,

$$\begin{aligned} E_g &= E_g^0 + 0.059 \log a_{\text{H}^+} \\ &= E_g^0 - 0.059 \text{ pH} \end{aligned} \quad (1)$$

For actual pH measurement, the glass electrode is standardised in buffer solutions of known pH values. Ionisation of a weak monobasic (HA) in aqueous solution may be represented as,

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of which the ionisation constant (K_a) is given by the activity quotient of the equilibrium (2):

$$K_a = \frac{a_{\text{H}^+} a_{\text{A}^-}}{a_{\text{HA}}} \quad (3)$$

where, a represents activity of the respective species which is related to the molar concentration, (c) according to $a = c.f.$, where f = activity coefficient. In dilute aqueous solutions of weak acids, ionic strength is very low, so the activity coefficients approach unity, hence, the concentrations approach activities. Consequently the ionisation constant (K_a) may be expressed as

$$K_a = [\text{H}^+][\text{A}^-] / [\text{HA}] \quad (4)$$

When a strong base NaOH is added to a weak acid acetic acid in an amount less than the stoichiometric requirement a buffer solution is formed, the pH of which is given by the Henderson's equation:

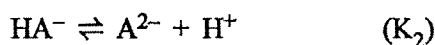
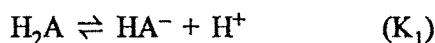
$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad (5)$$

If the amount of base added is just half-equivalent of the acid present, then $[\text{salt}] = [\text{acid}]$ and

$$\text{p}K_a = (\text{pH})_{1/2} \quad (6)$$

Where $(\text{pH})_{1/2}$ represents the pH of the solution at the half neutralization point. The $\text{p}K_a$ value of a weak acid is most conveniently determined pH metrically by titrating the weak acid with a strong base. A pH metric titration curve may be constructed by plotting the pH of the acid solution after each addition of the strong base and the equivalence point of the titration may be determined graphically. The pH of the solution corresponding to the half the neutralization point may be read out from the pH metric titration curve.

For dibasic acids like oxalic or succinic acid (H_2A), the ionization equilibria may be expressed as,



where K_1 and K_2 are dissociation constants for the first and second steps of dissociation, respectively.

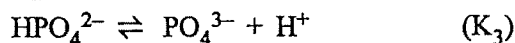
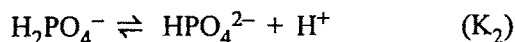
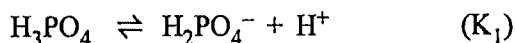
For oxalic/succinic acid, beyond the half-equivalence point the system is a buffer consisting of HA^- and A^{2-} . The pH of this buffer solution is given by

$$\text{pH} = \text{p}K_2 + \log \{ [\text{A}^{2-}] / [\text{HA}^-] \}$$

At $3/4$ th equivalence point $[\text{A}^{2-}] = [\text{HA}^-]$, hence, $(\text{pH})_{3/4} = \text{p}K_2$.

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A tribasic acid like phosphoric acid dissociates in three steps:



where, K_1 , K_2 and K_3 are the dissociation constants corresponding to the first, second and third steps of dissociation, respectively. Since both ratios K_1/K_2 and K_2/K_3 are greater than 10^4 , the titration curve against NaOH solution will show three inflexions.

At the first neutralisation point,

$$(\text{pH})_1 = \frac{1}{2} (\text{pK}_1 + \text{pK}_2)$$

Also, at the half of the first step of neutralisation,

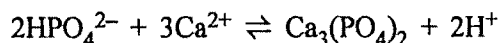
$$(\text{pH})_{1/2} = \text{pK}_1$$

Similarly at the second neutralisation point,

$$(\text{pH})_2 = \frac{1}{2} (\text{pK}_2 + \text{pK}_3)$$

From the above relations, we can find pK_1 , pK_2 , and pK_3 .

Titration should not be carried out till the third inflexion since the solution by that time becomes too alkaline ($\text{pH} \sim 10$) for the glass electrode to function properly. At this stage some solid CaCl_2 / BaCl_2 is added to the solution, then the pH of the solution comes down due to the release of H^+ ion :



The titration may now be continued to get the third inflexion.

Procedure:

1. Prepare 100 ml of a standard (N/20) solution of oxalic acid by accurate weighing in a digital balance.
2. Prepare 100 ml of (\sim N/2) NaOH solution.
3. Prepare 100 ml of (\sim N/20) acetic acid, succinic acid and phosphoric acid solution.
4. Prepare standard buffer solution of $\text{pH} = 4$ and $\text{pH} = 7$ by dissolving the corresponding pH tablets in the specified volume of distilled water.
5. Record the experimental temperature. Standardize the pH meter by alternately dipping the glass-calomel electrode assembly in $\text{pH} = 4$ and $\text{pH} = 7$ buffer solutions and adjusting the instrument accordingly at the experimental temperature.
6. Take 25 ml of (N/20) acetic acid solution in a 100 ml beaker. Add sufficient quantity of distilled water so that the combined electrode (glass-calomel assembly) dips into it properly. Allow the system to attain the equilibrium at the experimental temperature and record the pH.

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7. Add 2 drops of the (N/2) NaOH solution from a burette / micro burette stir gently to mix uniformly and record the pH. Repeat the process until the pH of the solution reads ~4.5. Then add 1 drop each time till the equivalence point is reached (indicated by sharp rise in pH). Record the pH and the number of drops of the titrant in a tabular form. Take a few more readings beyond the end point.
8. Determine the volume of 50 drops of the titrant solution and calculate the volume of one drop.
9. Repeat steps 6 and 7 for succinic acid/oxalic acid.
10. For phosphoric acid, addition of NaOH will continue till pH reaches around 10. After that, add some solid CaCl_2 / BaCl_2 , which will lower the pH of the solution around 4.5. Continue addition of NaOH solution till pH reaches around 9.
11. Plot, pH vs. number of drops (n) of the (~ N/2) NaOH solution added. From graph determine the number of drops of NaOH at equivalence point, and hence determine the strength of NaOH solution, and subsequently the same of acetic/dibasic/phosphoric acid solution. Graphically determine the different pK values of the various acids.

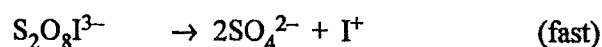
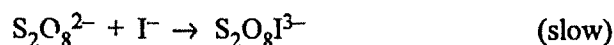
Experiment No 9 : To study the kinetics of the reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- by colourimetric method.

Theory:

The overall reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- is



The probable mechanism is,



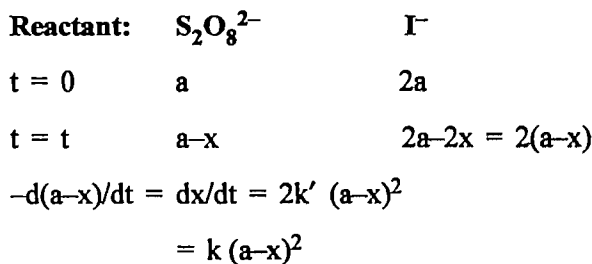
The reaction (1) is found experimentally to be a second order reaction, being first order in $[\text{S}_2\text{O}_8^{2-}]$ and first order in $[\text{I}^-]$, and the rate law may be expressed according to

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{I}^-]}{dt} = -\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = \frac{d[\text{I}_2]}{dt} = k' [\text{S}_2\text{O}_8^{2-}] [\text{I}^-] \quad (2)$$

where, k' = second order rate constant in $\text{L mol}^{-1}\text{s}^{-1}$.

If $[\text{S}_2\text{O}_8^{2-}]$ and $[\text{I}^-]$ are taken in their stoichiometric mole ratio of 1:2 then for a fixed volume of reaction mixture (say 1 L), then If a mol L^{-1} is the initial concentration of $\text{S}_2\text{O}_8^{2-}$ and $x \text{ mol L}^{-1}$ of $\text{S}_2\text{O}_8^{2-}$ has reacted by the time t , their amounts vary with time as follows:

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where $k = 2k'$. Since at $t = 0$, $x = 0$ and at $t = t$, $x = x$, the eqn. (3) on integration takes the form (4)

$$\frac{x}{a(a-x)} = kt \quad (4)$$

Since only one of the substances involved, I_2 , is coloured ($\lambda_{\text{max}} = 525 \text{ nm}$), its absorbance A_t at any instant of time (t) proportional to its concentration (x), provided Beer's Law is obeyed. The eqn. (4) is then transformed to:

$$kt = \frac{1}{a} \frac{A_t}{A_\infty - A_t} \quad (5)$$

where A_t and A_∞ are the absorbance values at $t = t$ and $t = \infty$ respectively. On rearrangement, one obtains,

$$\frac{1}{A_t} = \frac{1}{A_\infty} + \frac{1}{akA_\infty} \cdot \frac{1}{t} \quad (6)$$

Thus, a plot of $(1/A_t)$ against $(1/t)$ will give a straight line with intercept equal to $(1/A_\infty)$ and slope equal to $(1/akA_\infty)$ from which the value of the rate constant, k , may be evaluated using the relation:

$$k = (\text{intercept}) / (a \times \text{slope}).$$

Procedure :

1. Prepare 100 ml of a standard (N/10) $\text{K}_2\text{Cr}_2\text{O}_7$ and 100 ml of a standard KI (strength $> \text{N}/10$) solutions by accurate weighing. Prepare 100 ml of a $\text{K}_2\text{S}_2\text{O}_8$ solution ($> \text{N}/10$) and 250 ml of a (N/10) sodium thiosulfate solution by weighing with a rough balance.
2. Standardize the thiosulfate solution against the standard (N/10) dichromate following the usual procedure.
3. Take 10 ml of the prepared $\text{K}_2\text{S}_2\text{O}_8$ solution in a 250 ml conical flask, add 10 ml of 10% (w/v) KI solution and 2 ml of glacial acetic acid. Cover the conical flask with watch glass and keep the mixture in dark for 25 ~ 30 minutes. Add 80 ml distilled water and then

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titrate the liberated iodine with the standard ($\sim N/10$) thiosulfate solution using starch indicator. Calculate the strength of the $K_2S_2O_8$ solution. Prepare an exact ($N/10$) $K_2S_2O_8$ solution by accurate dilution this solution.

4. Similarly prepare an exact ($N/10$) KI solution by exact dilution of the prepared standard ($> N/10$) KI solution.
5. Mix the $K_2S_2O_8$ and KI solutions as follows, one at a time, and note the time of half discharge of any one of the reactants in each case.

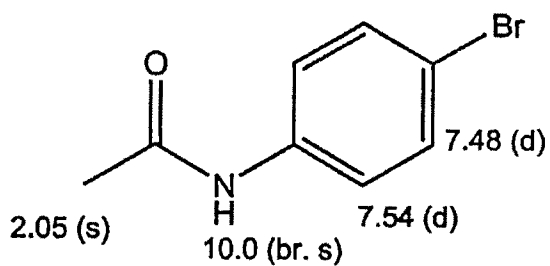
	($N/10$) KI solution (ml)	($N/10$) $K_2S_2O_8$ (ml)
Set Composition	10	10

6. Record the absorbance (A) of the solution at 525 nm wavelength at an interval of about 1 minute. Record the experimental temperature.
7. Plot $1/A_t$ against $1/t$ and find k from the slope and intercept of the resulting straight line.

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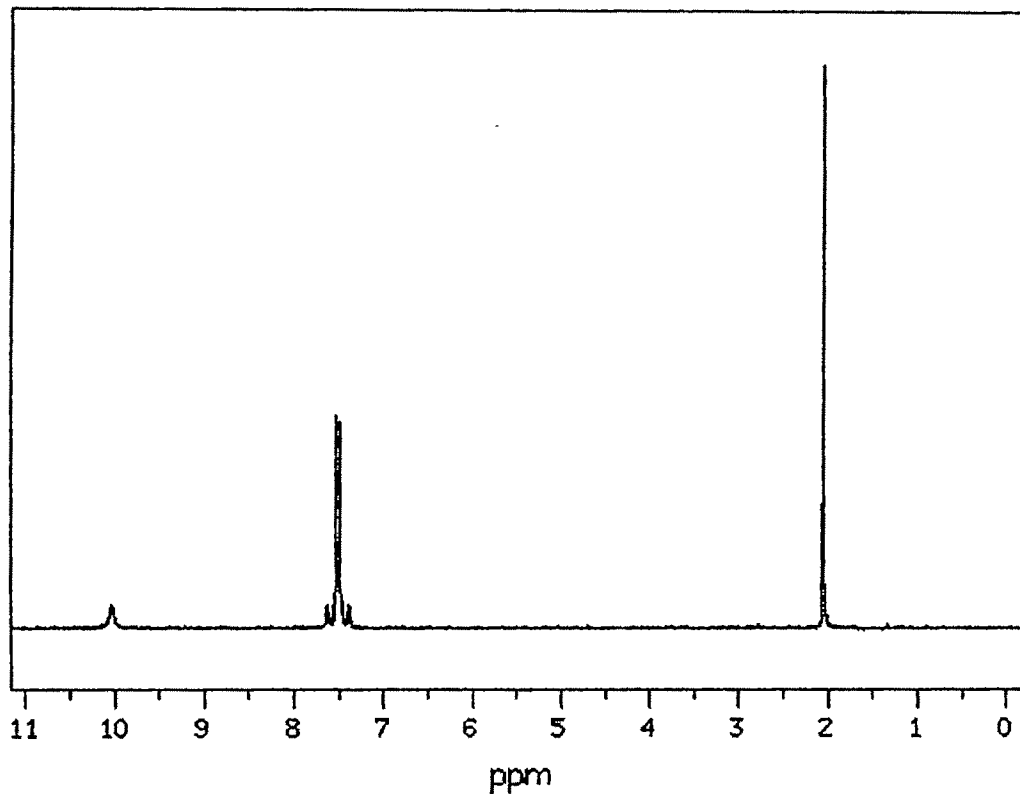
Spectroscopic Analysis of Organic Compounds

^1H NMR of *p*-Bromoacetanilide

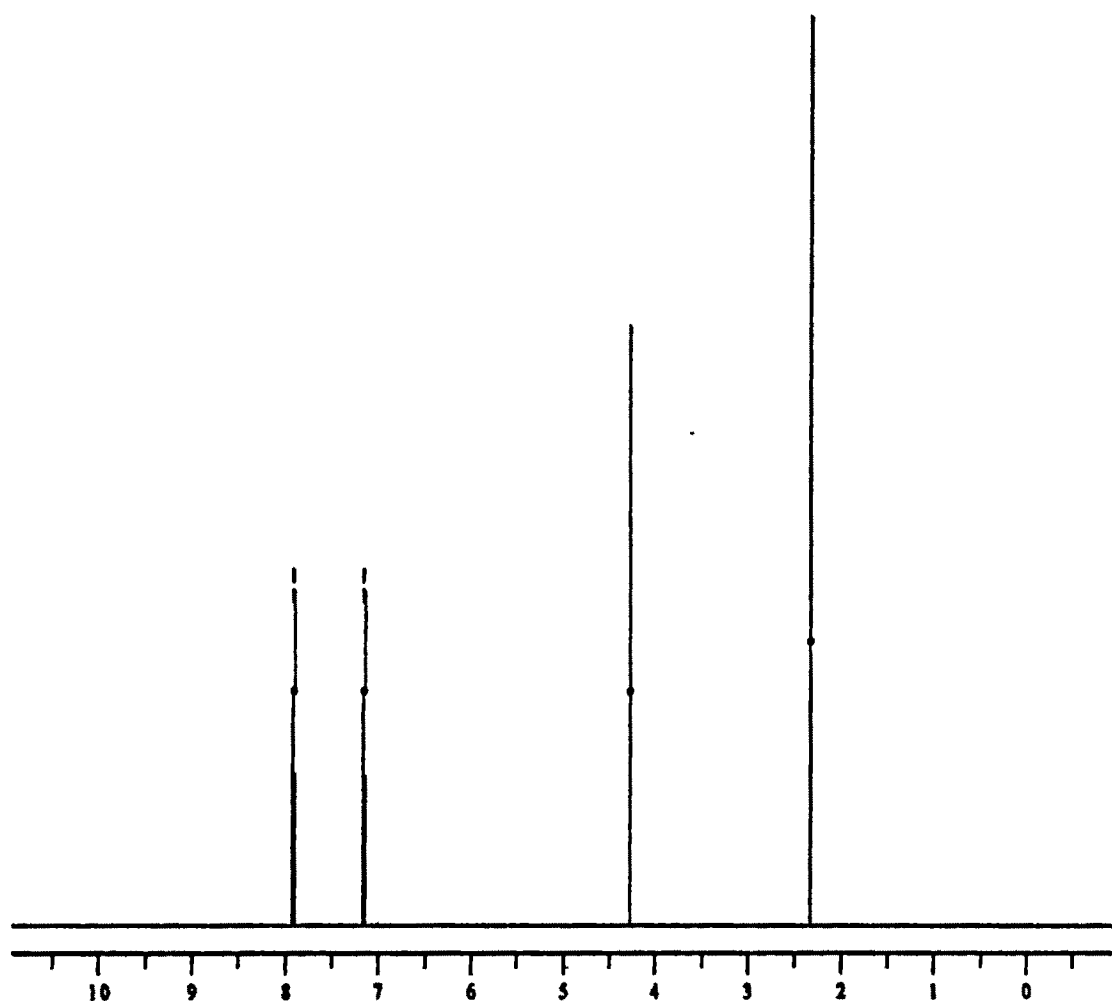
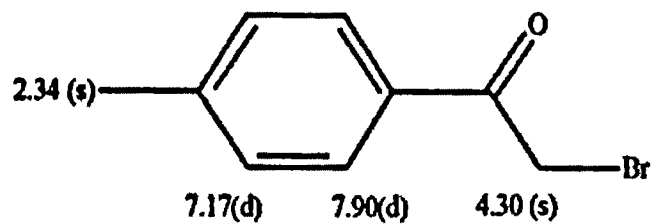


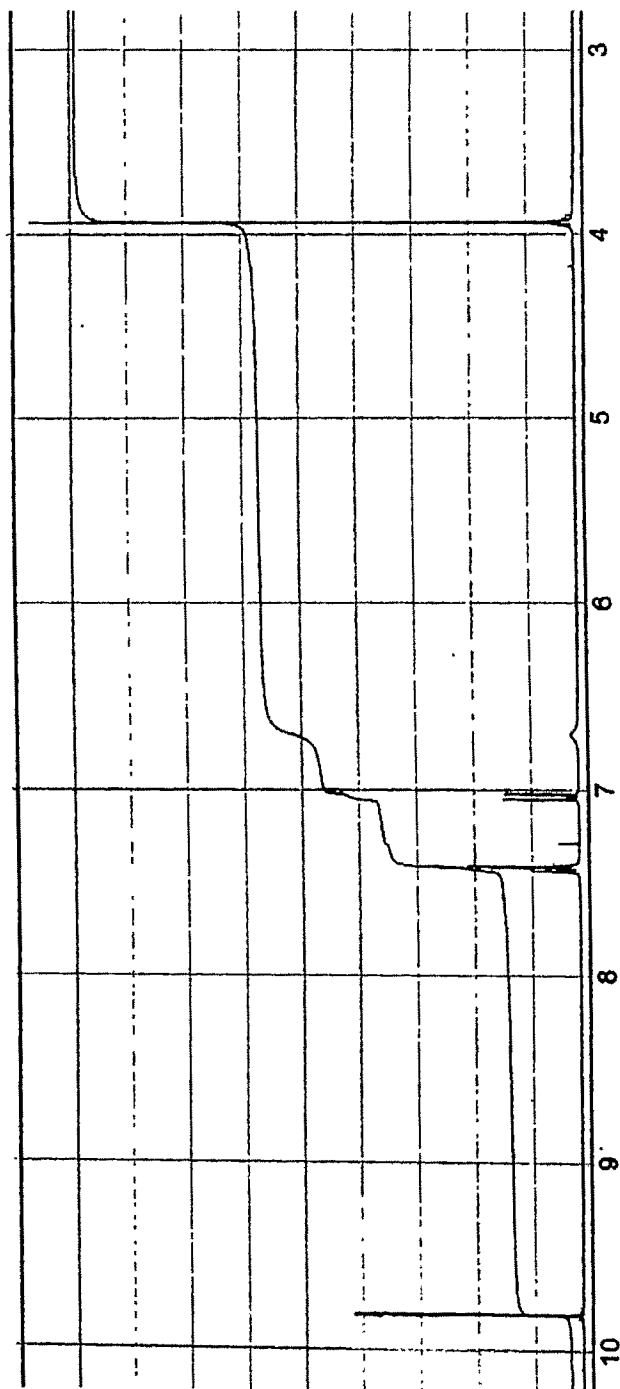
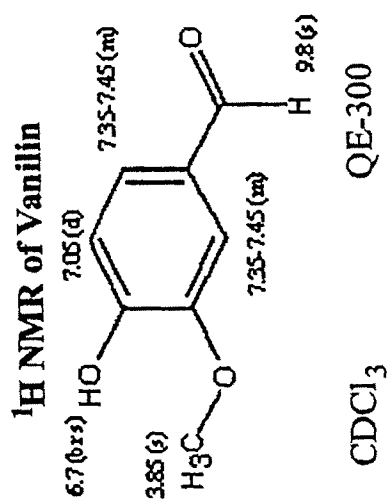
89.56 MHz

0.048 g : 0.5 ml $\text{DMSO}-d_6$

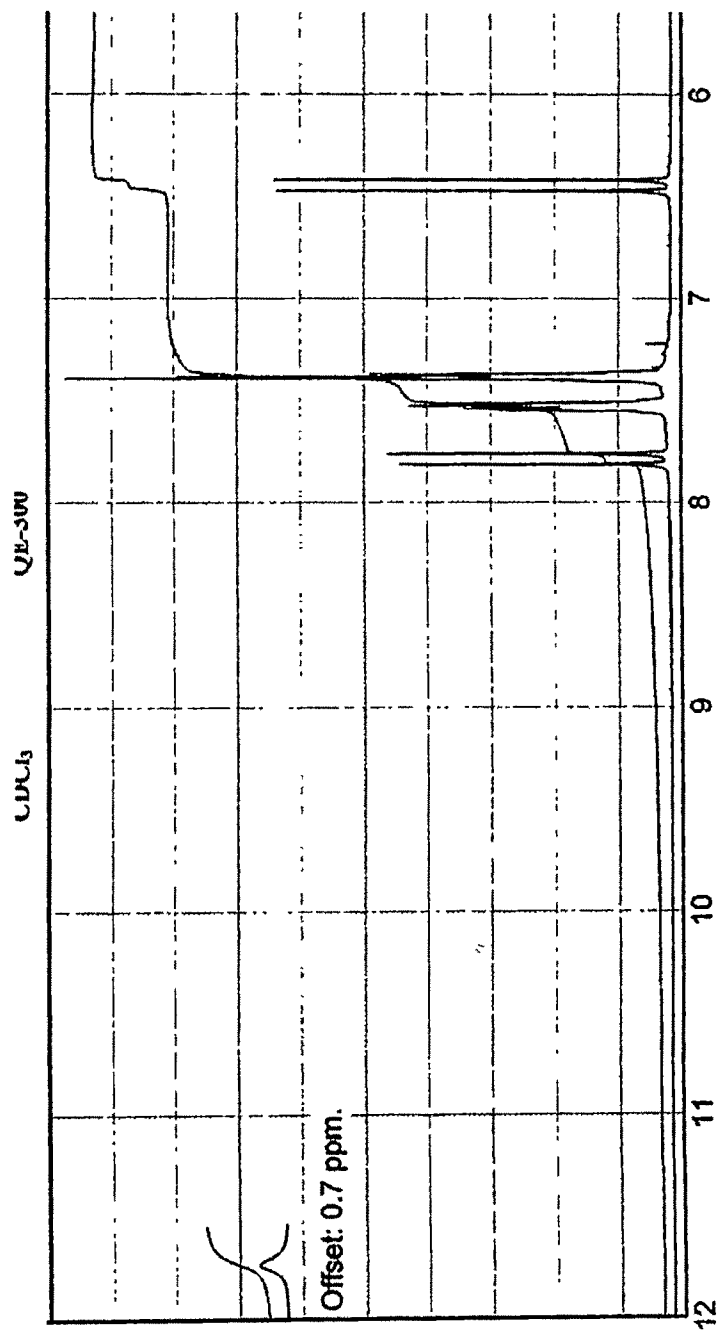
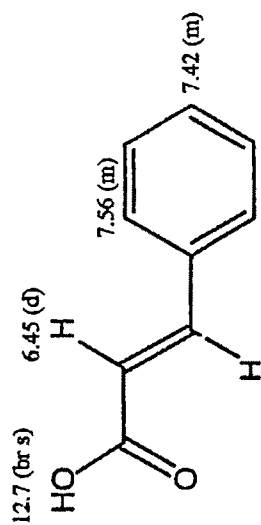


¹H NMR of 4-Methyl- α -bromoacetophenone



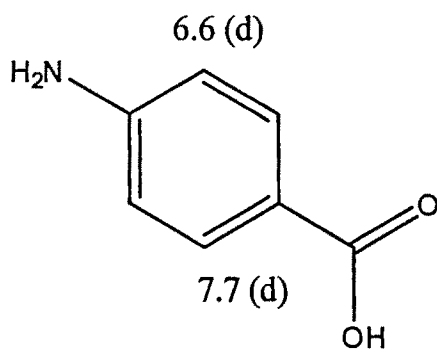


^1H NMR of *trans*-Cinnamic acid

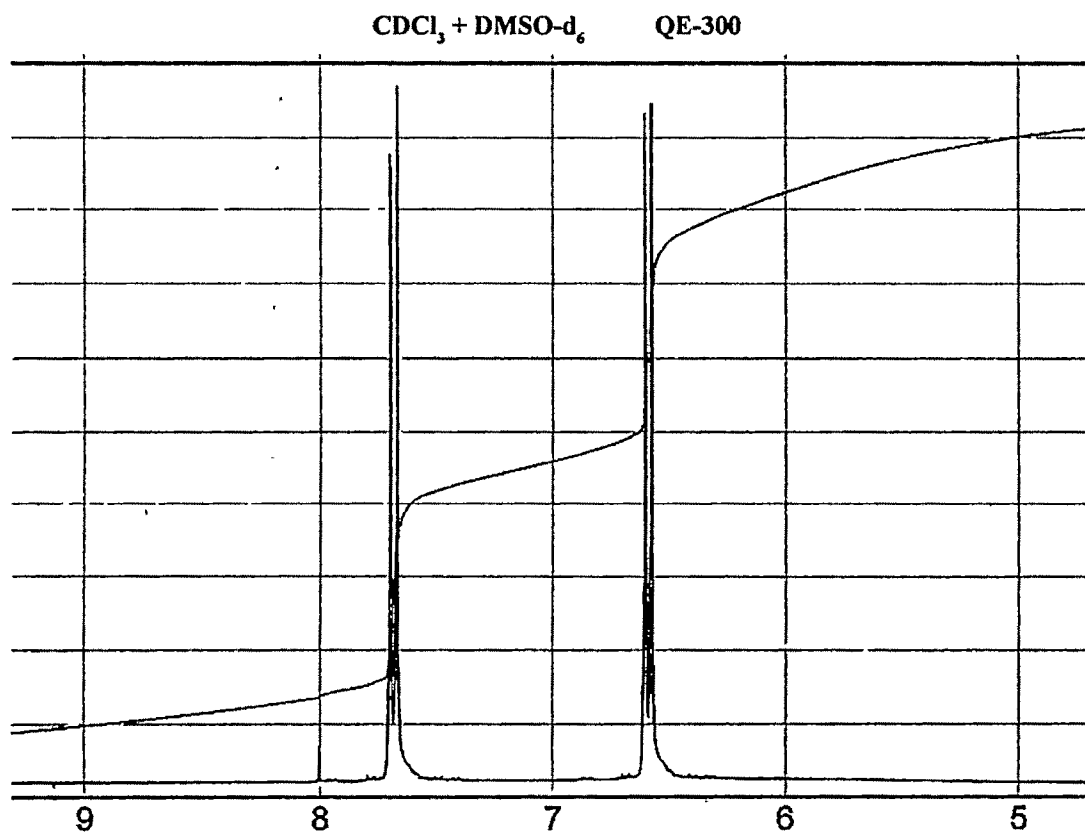


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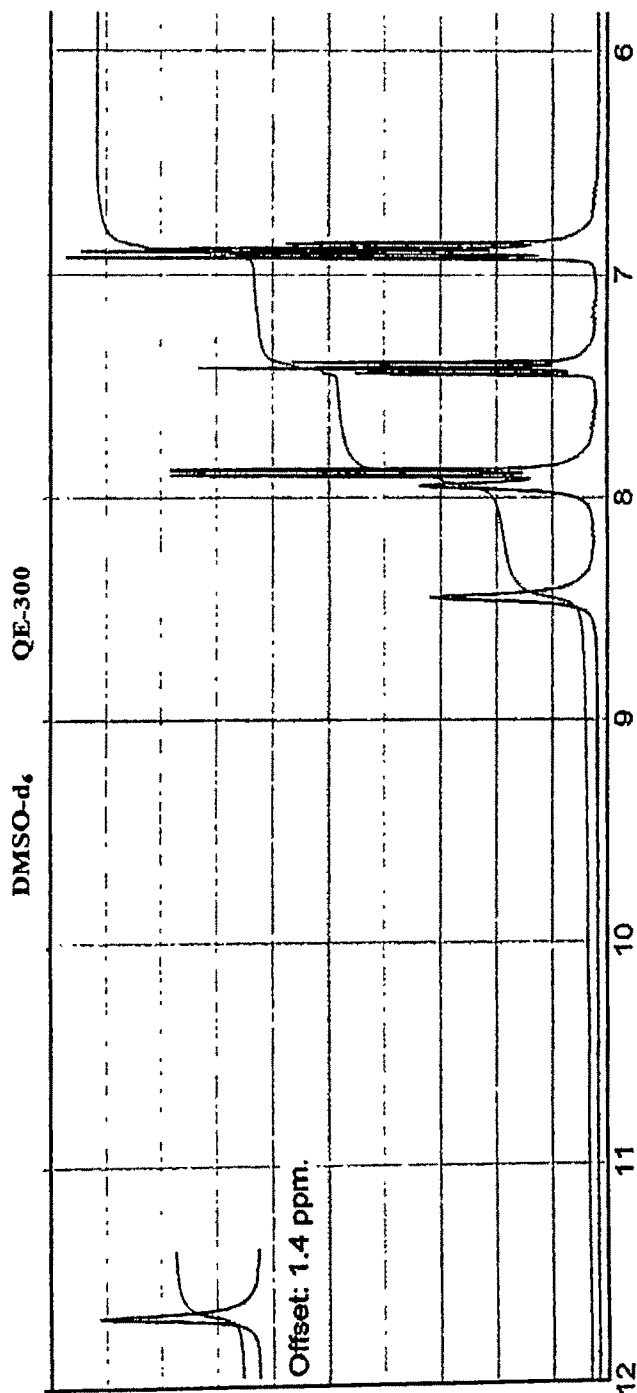
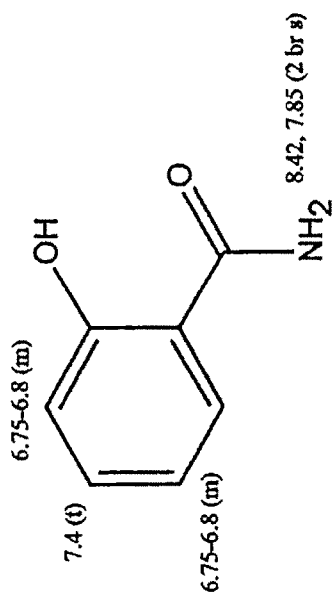
^1H NMR of *p*-Aminobenzoic acid (4-Aminobenzoic Acid)

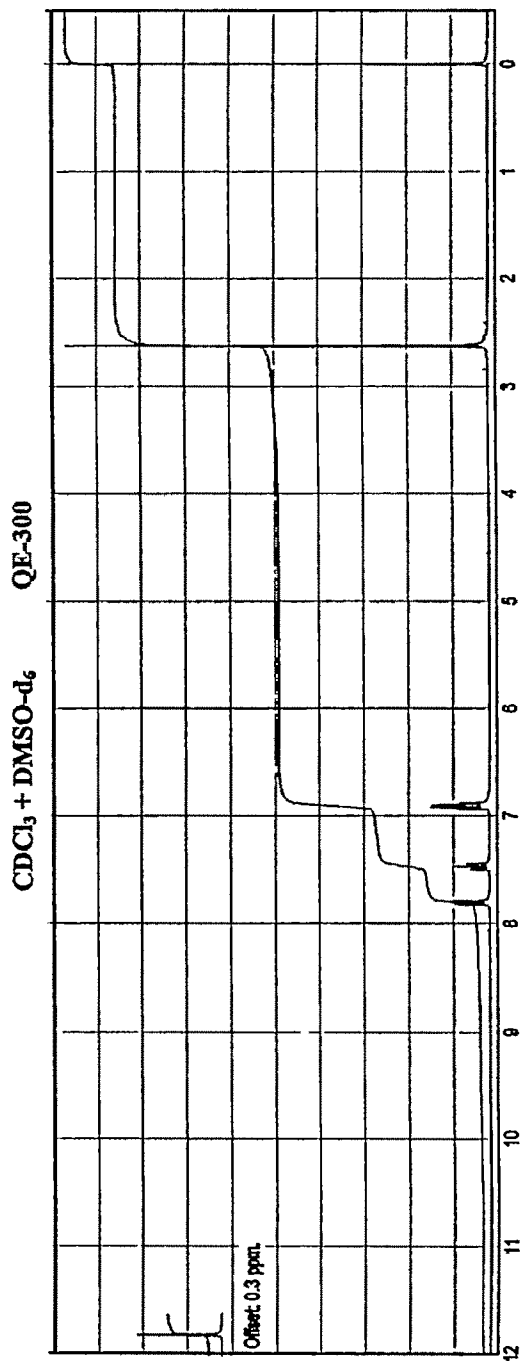


Offset : 3.0 ppm

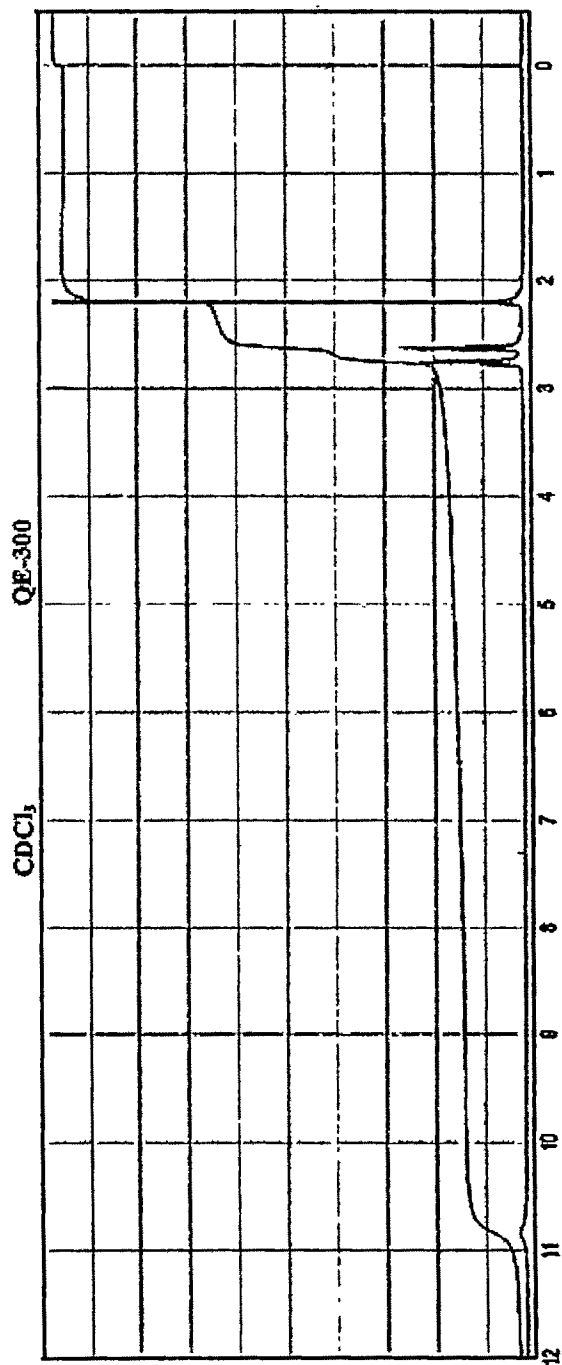
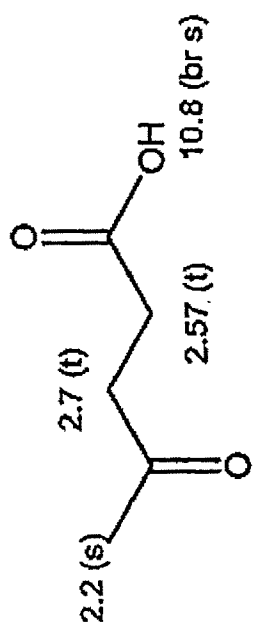


¹H NMR of Salicylamide

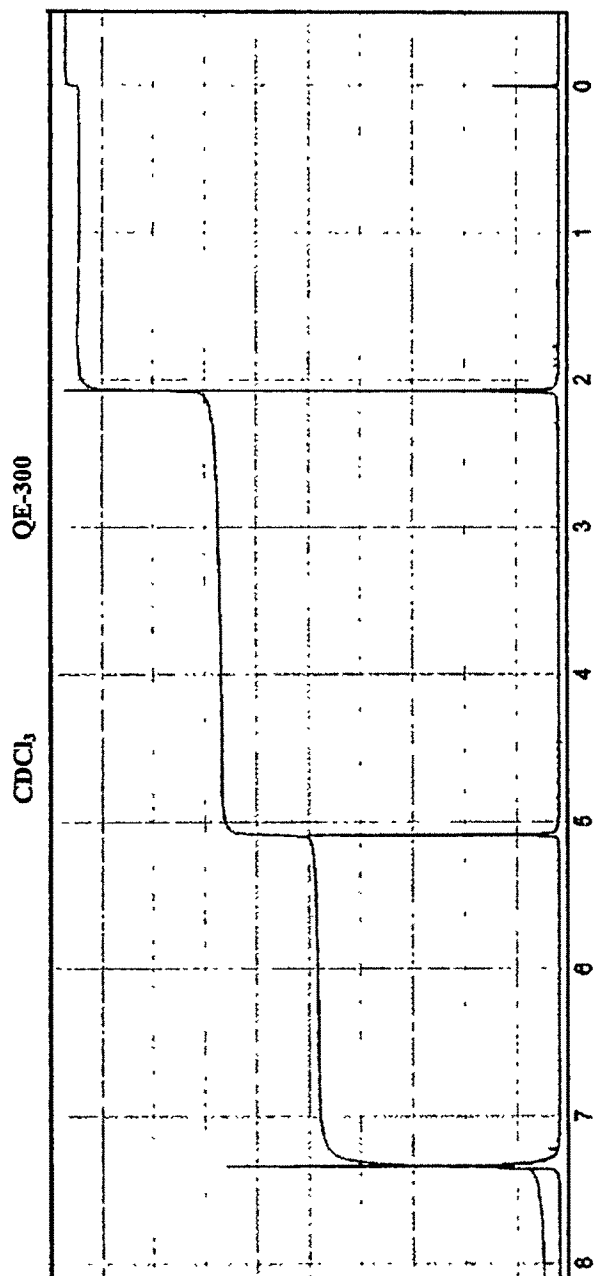
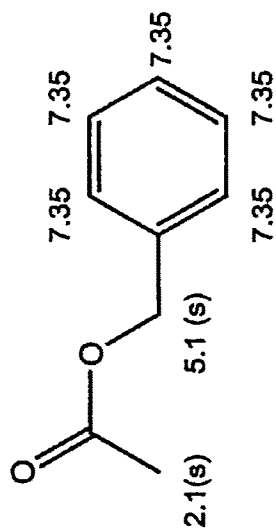


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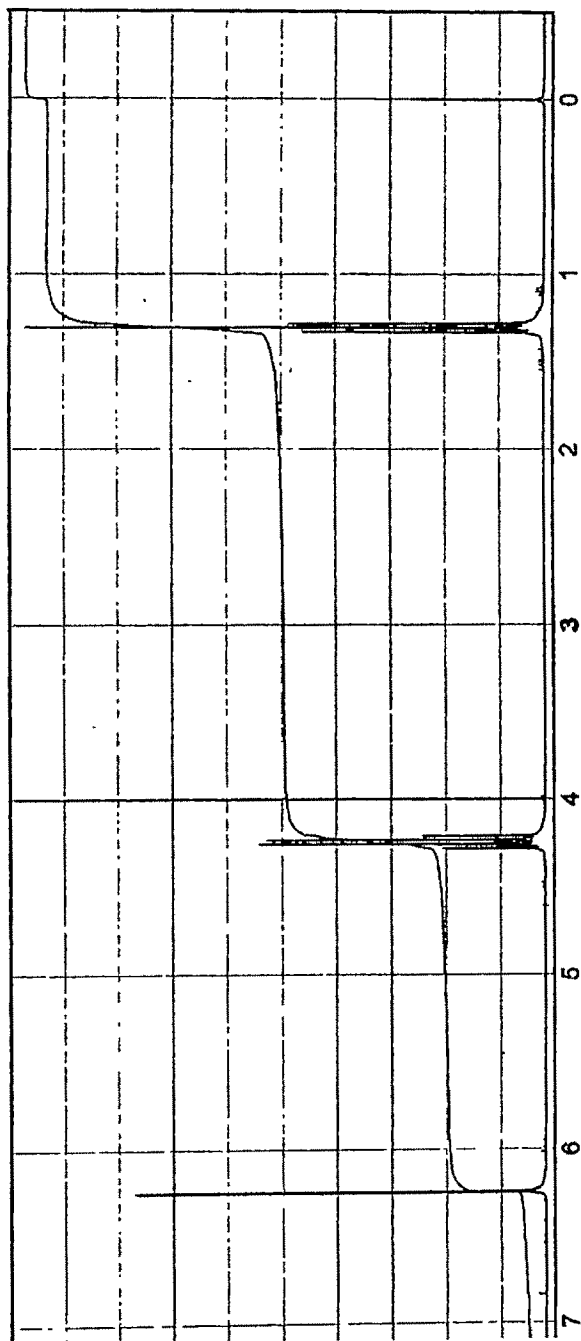
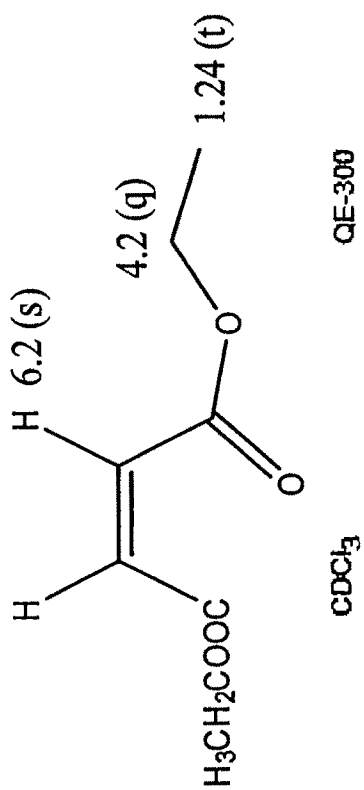
¹H NMR of Laevulinic Acid (4-Oxopentanoic Acid) (4-Ketopentanoic Acid)



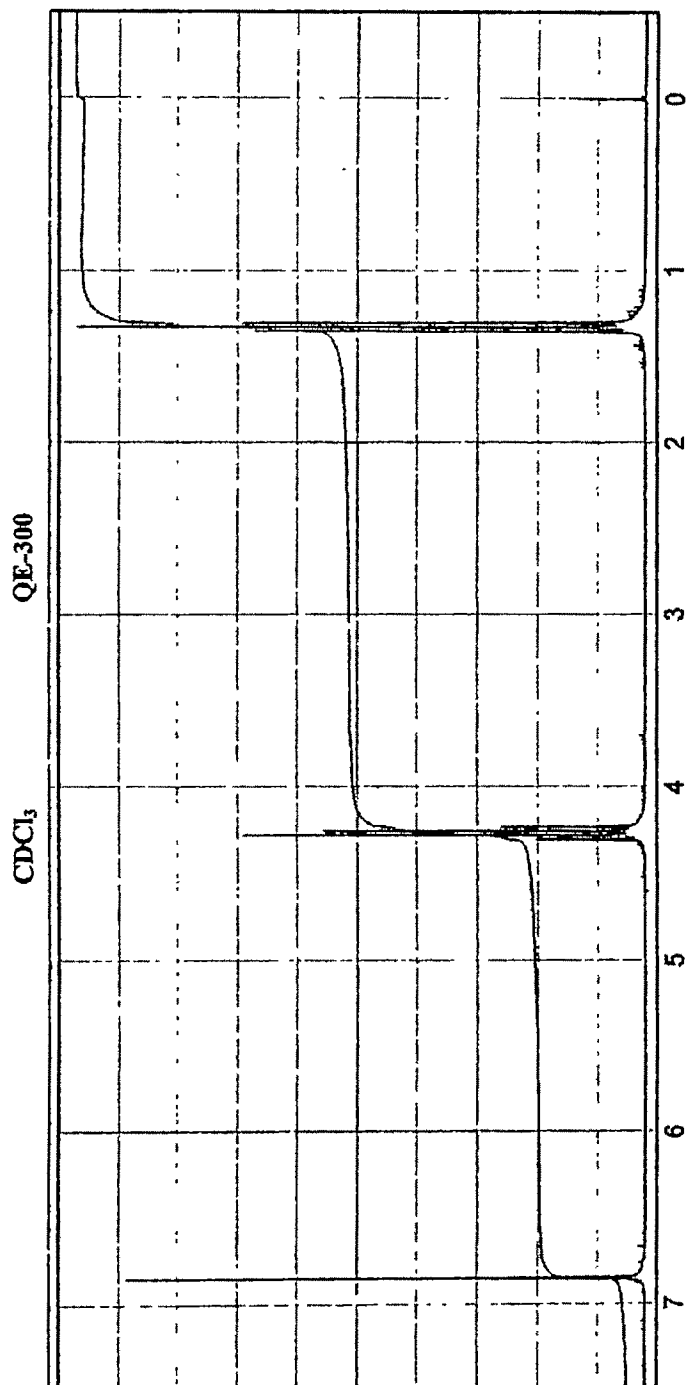
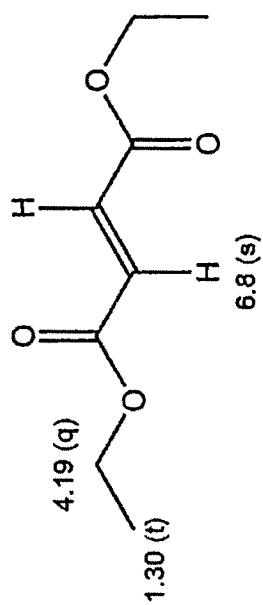
¹H NMR of Benzyl Acetate



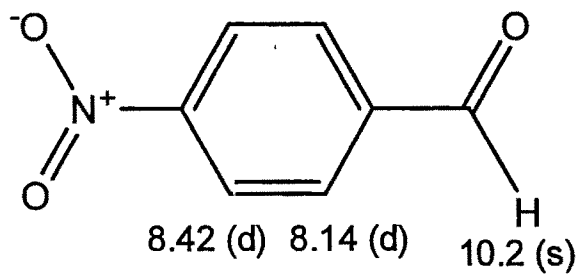
¹H NMR of diethyl maleate



¹H NMR of Diethyl Fumarate

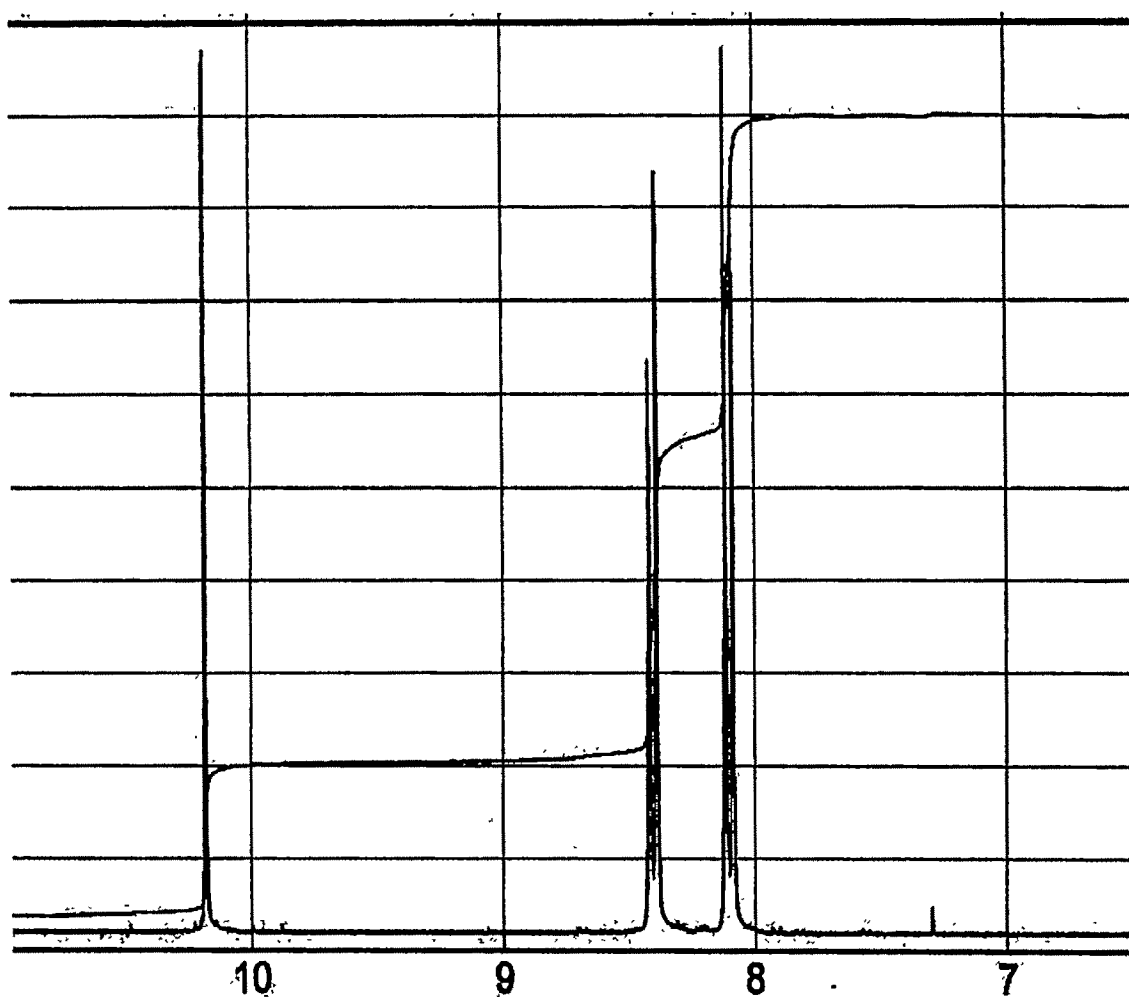


¹H NMR of 4-Nitrobenzaldehyde (*p*-Nitrobenzaldehyde)

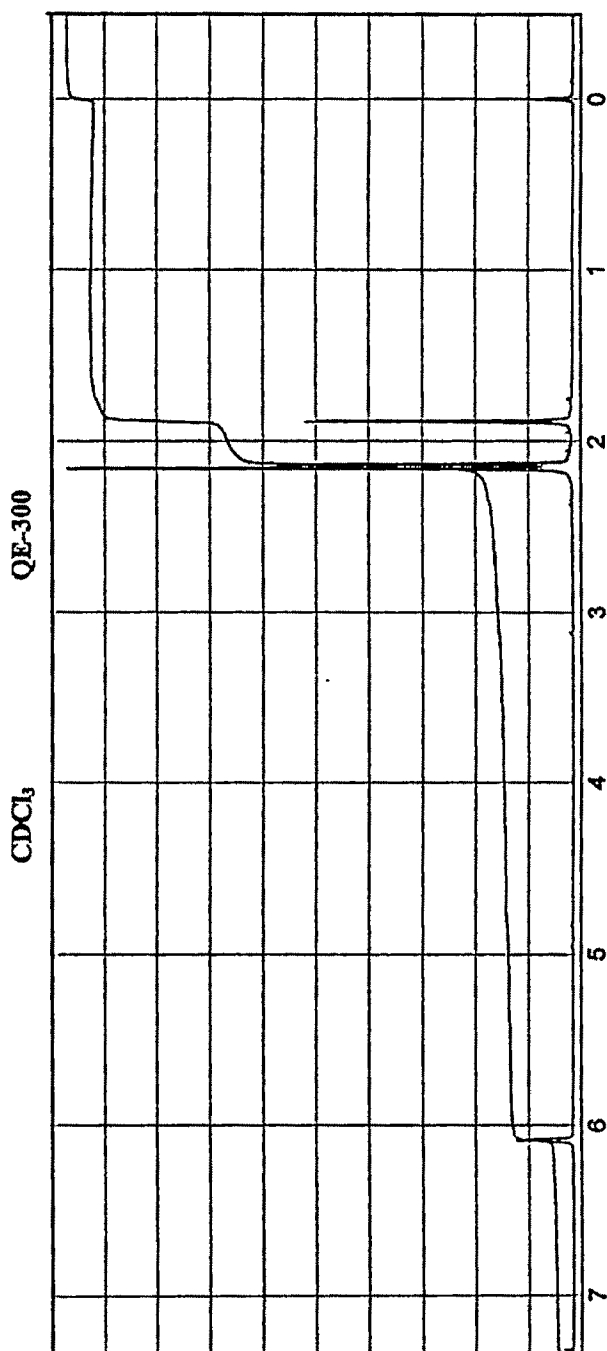
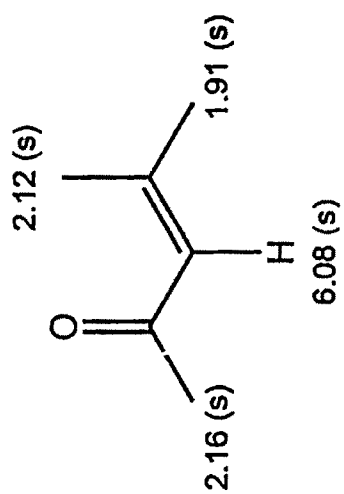


CDCl₃

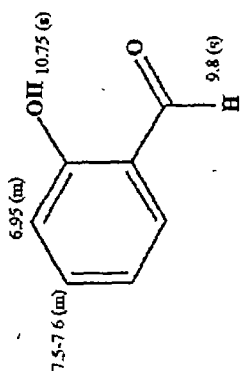
QE-300



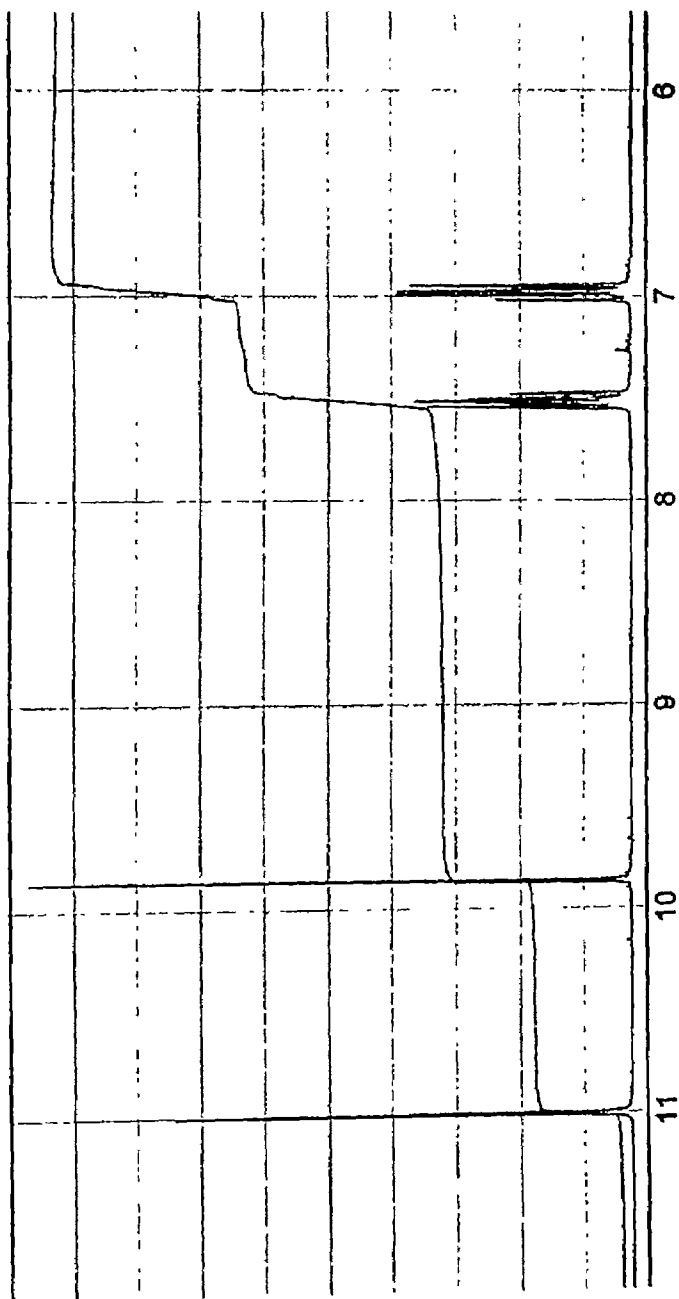
¹H NMR of Mesityl Oxide



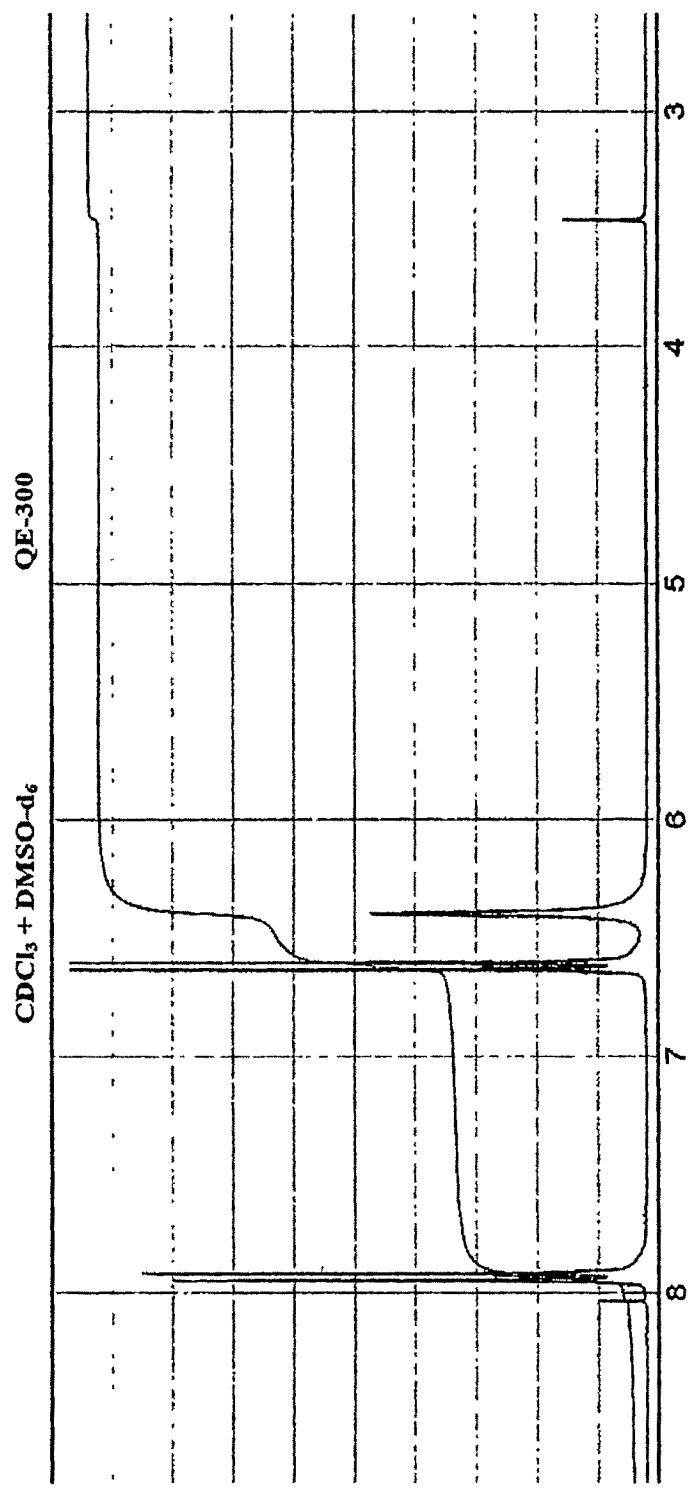
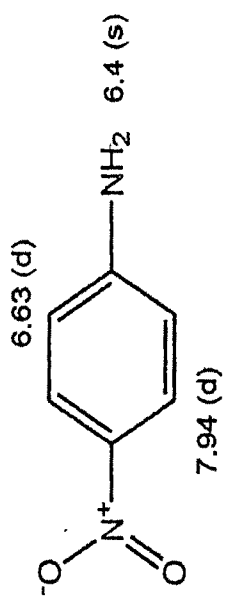
¹H NMR of Salicylaldehyde



CDCl₃ QE-300

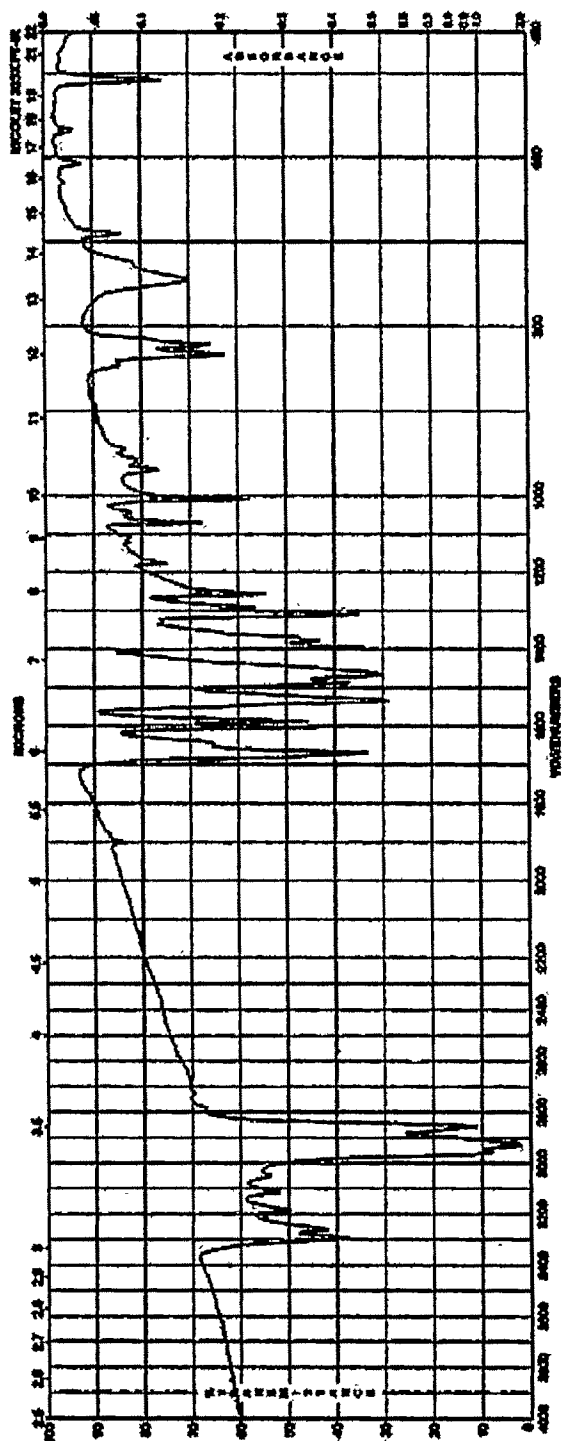


¹H NMR of 4-Nitroaniline (*p*-Nitroaniline)



p-Bromobenzamide:

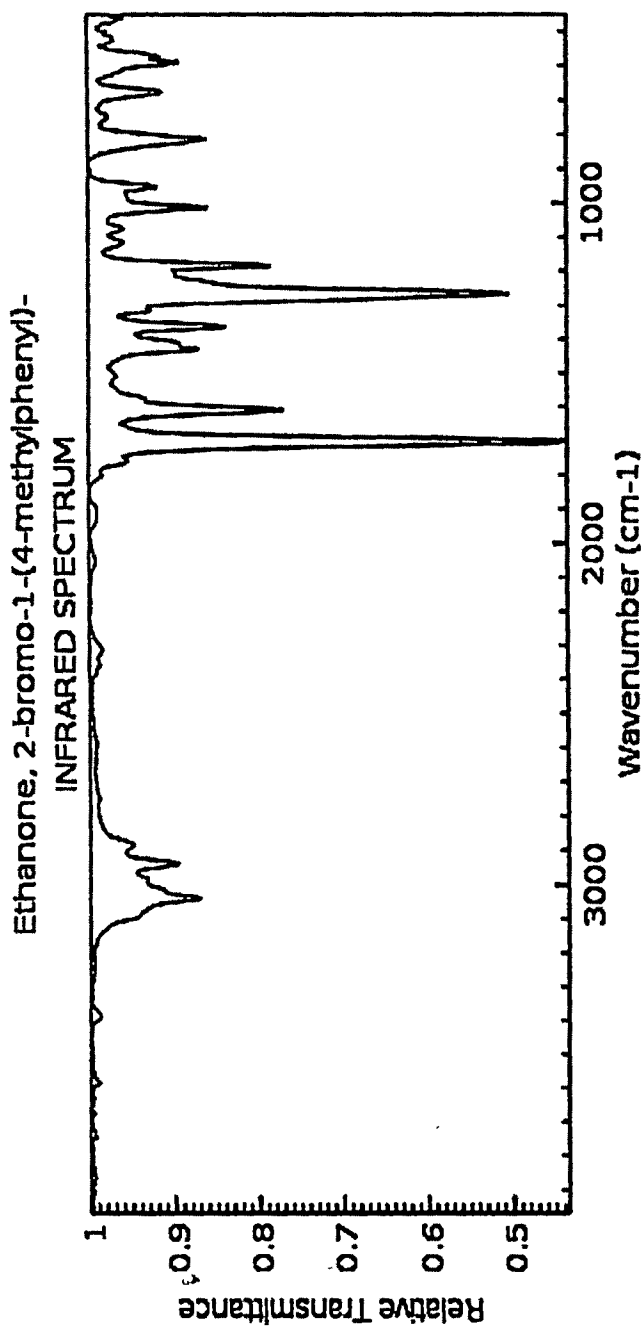
FT-IR (CCl₄) 3300 (N-H st.), 2950, 2850 (sp² & sp³ C-H st), 1680 (C=O amide I),
1540 (amide II), 1600, 1470 (C=C st. aromatic)
*[520 (C-Br st.) cm⁻¹.]



*N.B. : Vibrations not included in the syllabus.

4-Methyl- α -bromoacetophenone:

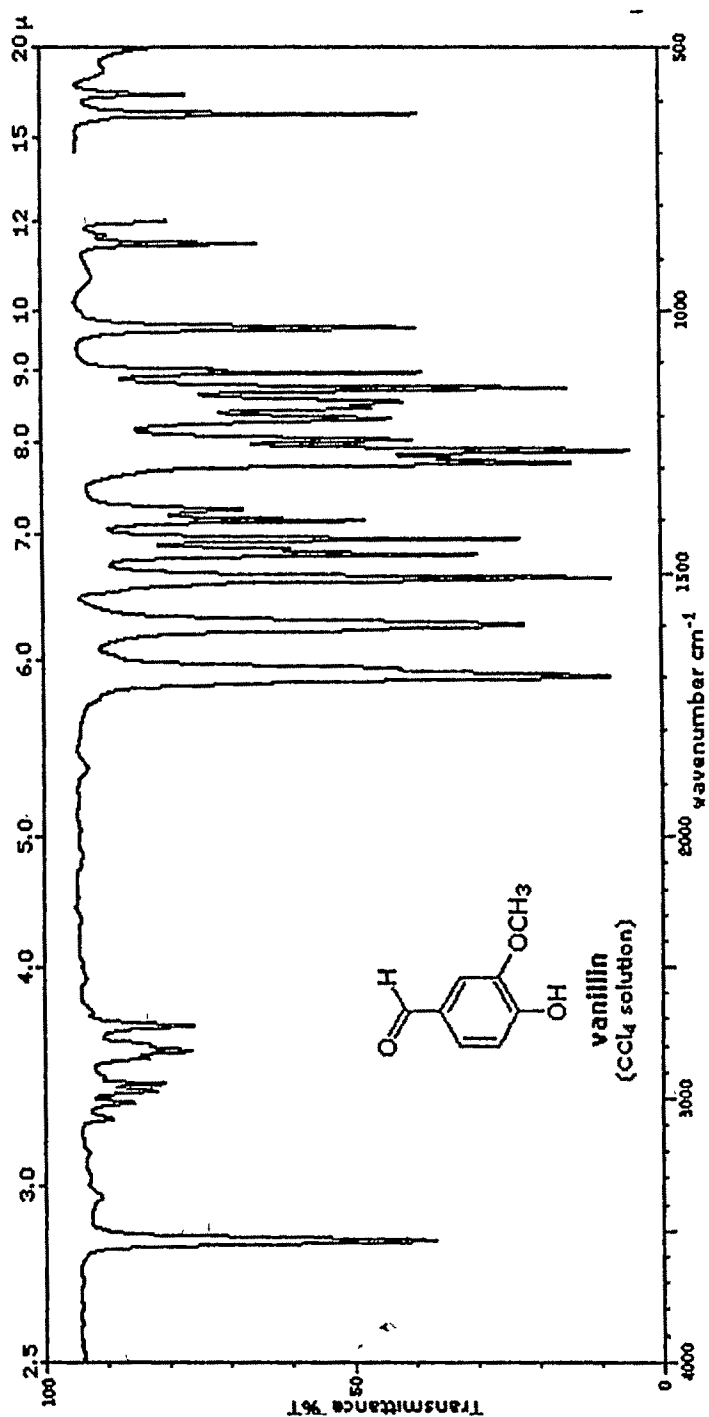
FT-IR (CCl_4) 3050, 2975 (C-H st.), 1710 (C=O st.), 1600(Ar- C=C st), *[825 (*para*-disubstituted benzene), 520 (C-Br st.)] cm^{-1} .



*N.B. : Vibrations not included in the syllabus.

Vanillin:

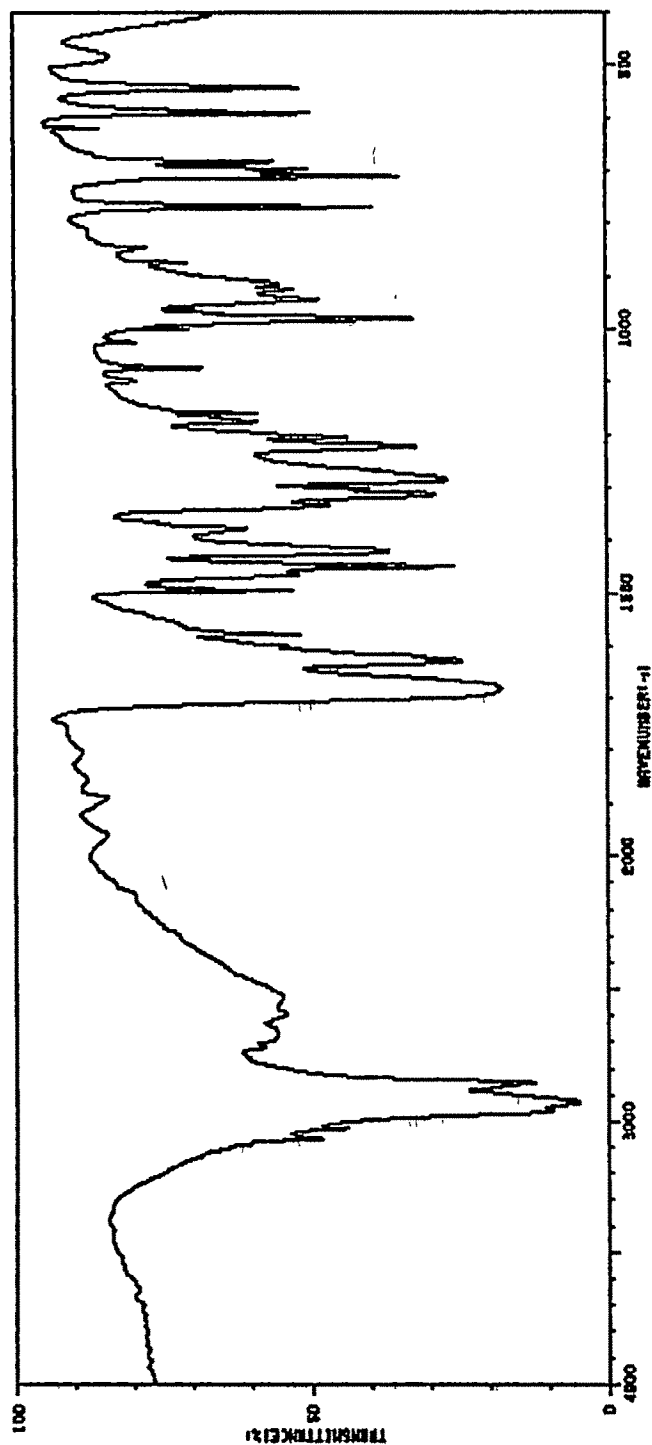
FT-IR (CCl_4) 3550 (O-H st.), 3100-2950(sp^2 C-H and sp^3 C-H st overlapping), 2850 & 2750 (C-H st.of -CHO), 1700 (C=O st.), 1600, 1520 (Ar C=C), *[1150 (C-O st.)] cm^{-1} .



*N.B. : Vibrations not included in the syllabus.

trans-Cinnamic acid:

FT-IR (CCl_4) 3070-2520 (br. O-H st.), 1680 (C=O st.), 1620 (C=C st, conjugated), 1580, 1520 (sp^2 C=C st. aromatic)* [970 (C-H def. *trans* alkene), 760, 710 (C-H o.o.p bending of monosubstituted benzene)] cm^{-1} .

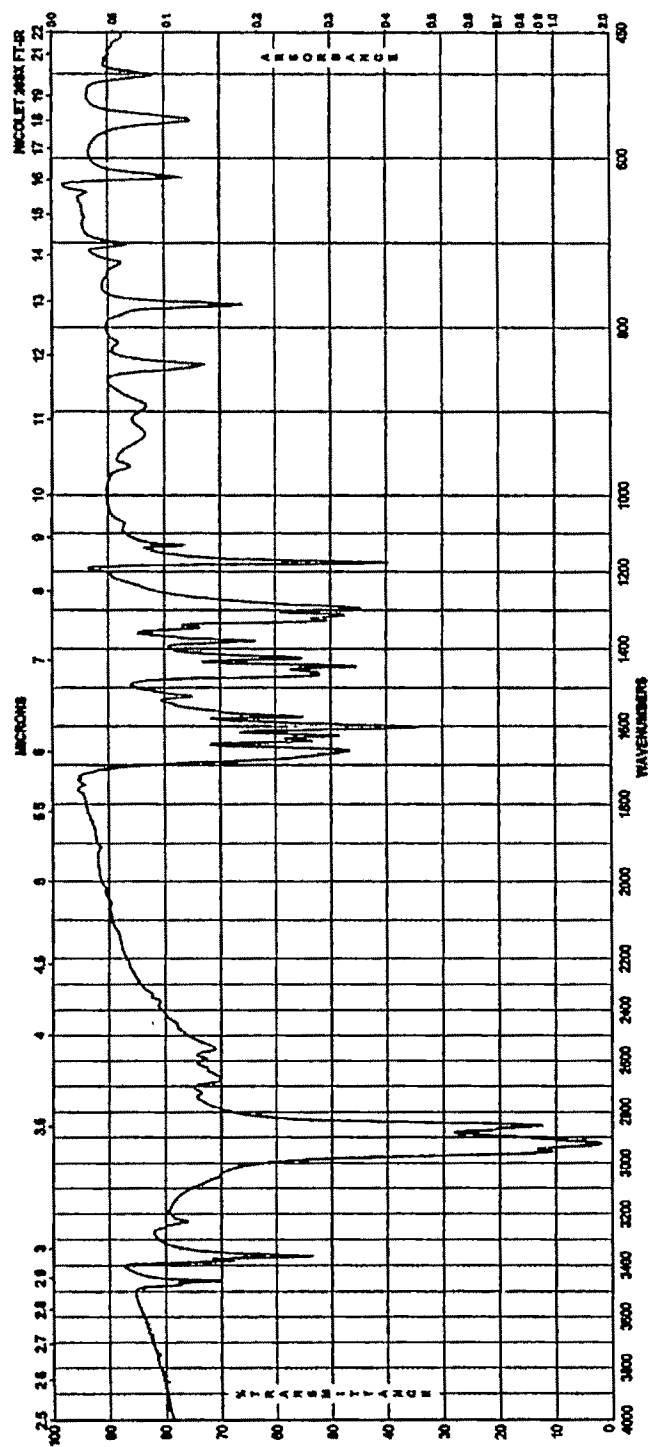


*N.B. : Vibrations not included in the syllabus.

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p-Aminobenzoic Acid (4-Aminobenzoic Acid):

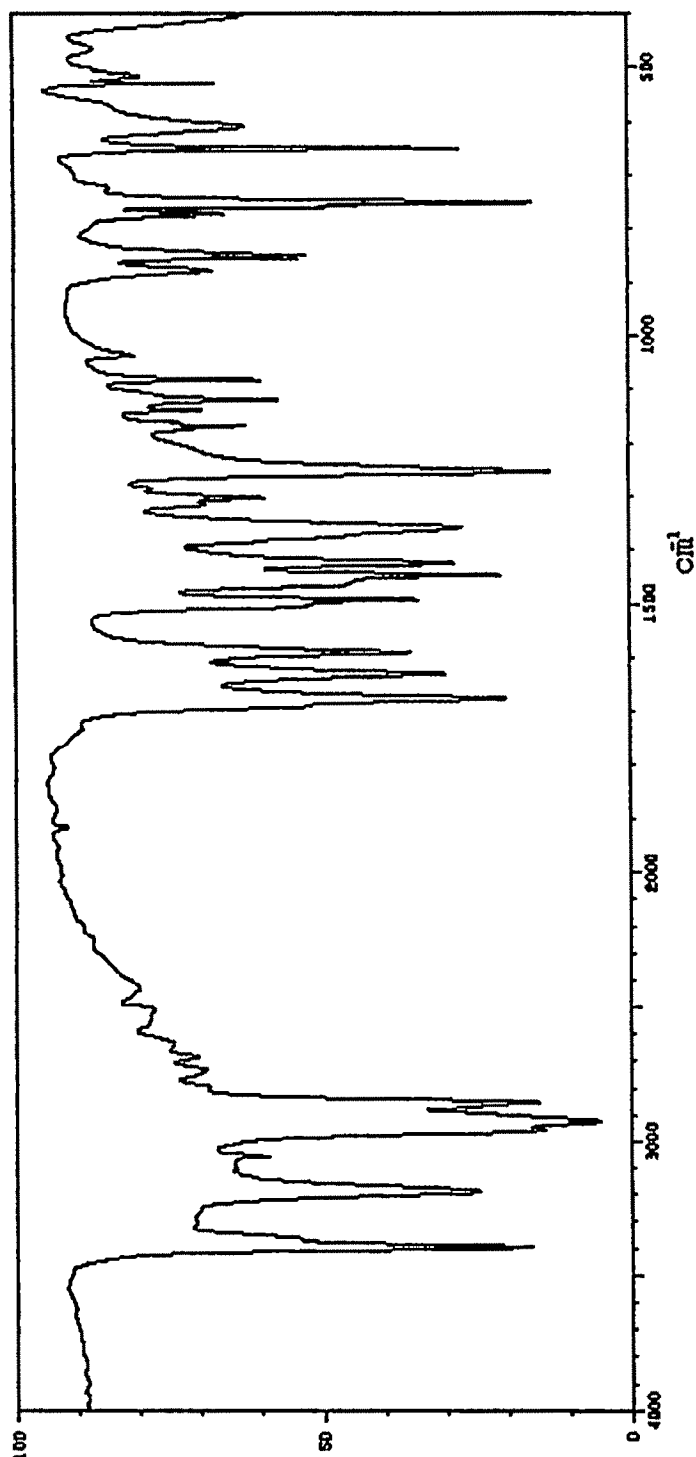
FT-IR (CCl_4) 3460 & 3360 (N-H st.), 2930, 2860 (C-H st.), 2700-2500 (O-H st.) 1670 (C=O st.), 1600, 1430 (C=C), *[850 (*p*-disubstituted benzene)] cm^{-1} .



*N.B. : Vibrations not included in the syllabus.

Salicylamide:

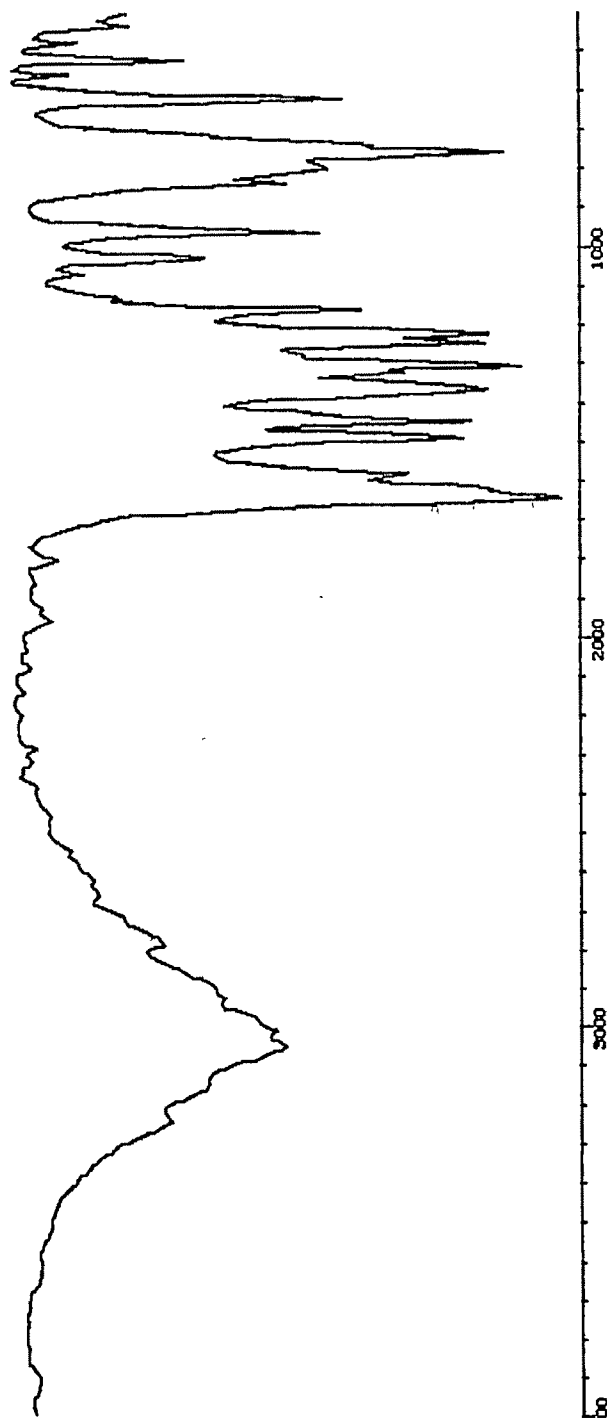
FT-IR (CCl_4) 3400 & 3200 (N-H st.), 2900 (C-H st.), 1680 (C=O st.), 1620, 1500 (Ar-C=C st), 1580 (N-H bend amide II), *[1420 (C-N st.), 1250 (C-O st.), 750 (o-disubstituted benzene)] cm^{-1} .



*N.B. : Vibrations not included in the syllabus.

2-Hydroxyacetophenone:

FT-IR (CCl_4) 3200-2850(br. O-H st.), 1650 ($\text{C}=\text{O}$ st.), 1580, 1500 ($\text{Ar}-\text{C}=\text{C}$ st.),
*[1240 ($\text{C}-\text{O}$ st.), 760 (*o*-disubstituted benzene)] cm^{-1} .

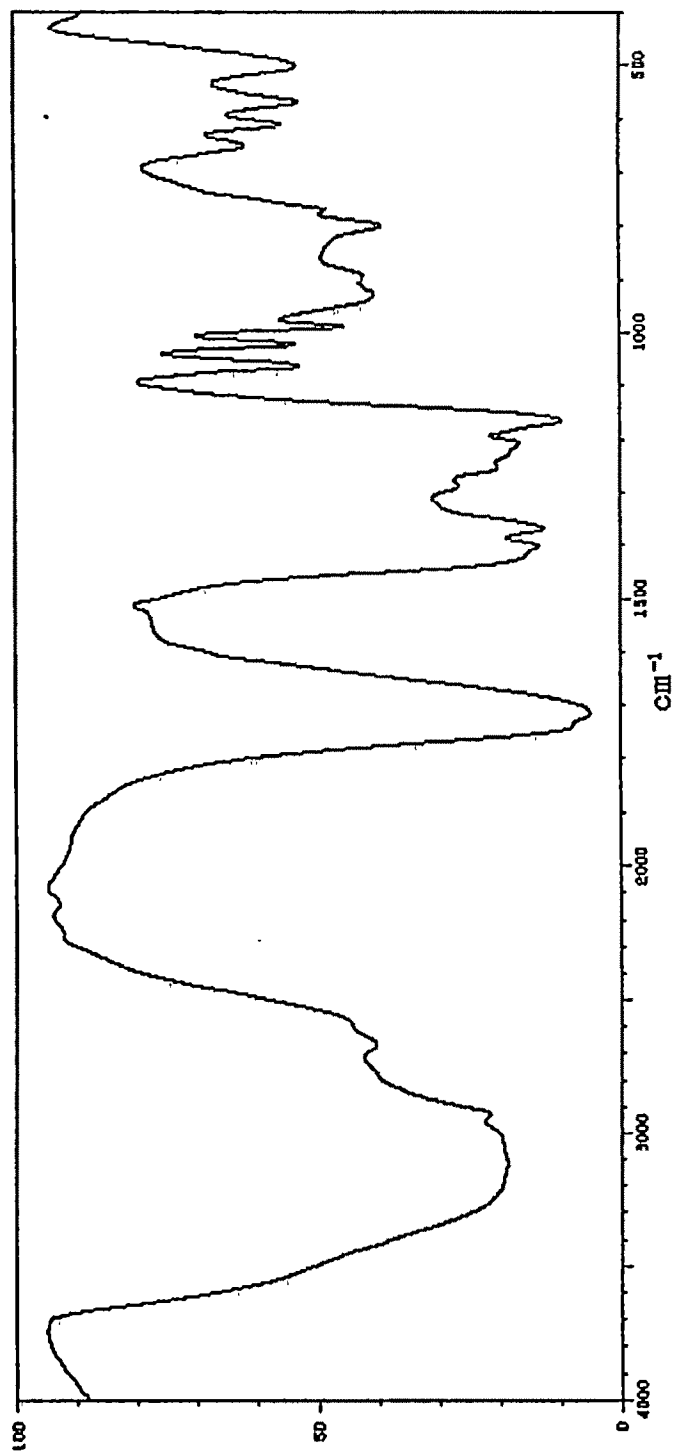


***N.B. : Vibrations not included in the syllabus.**

4-Ketopentanoic acid (4-Oxopentanoic Acid) (Laevulinic Acid):

FT-IR (CCl₄) 3300-29000 (br. O-H st.), 2700 (C-H st.), 1750 & 1715 (C=O st.),

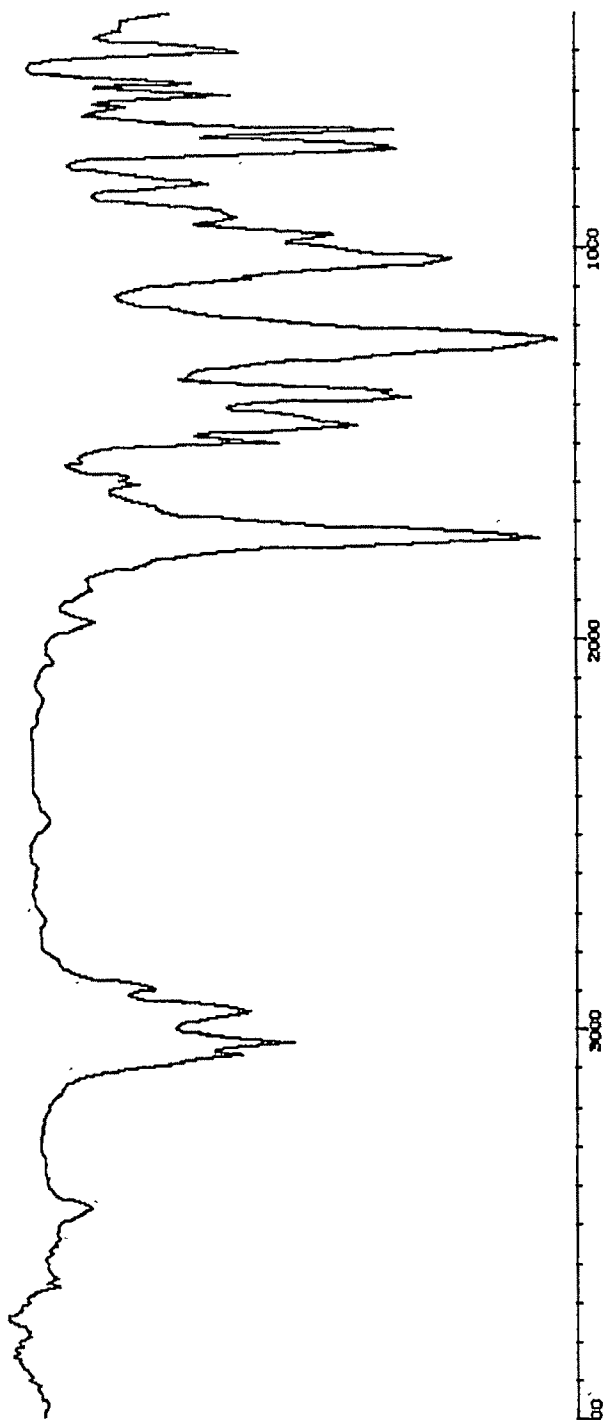
*[1430 & 1370 (CH₂ bending)] cm⁻¹.



*N.B. : Vibrations not included in the syllabus.

Benzyl Acetate:

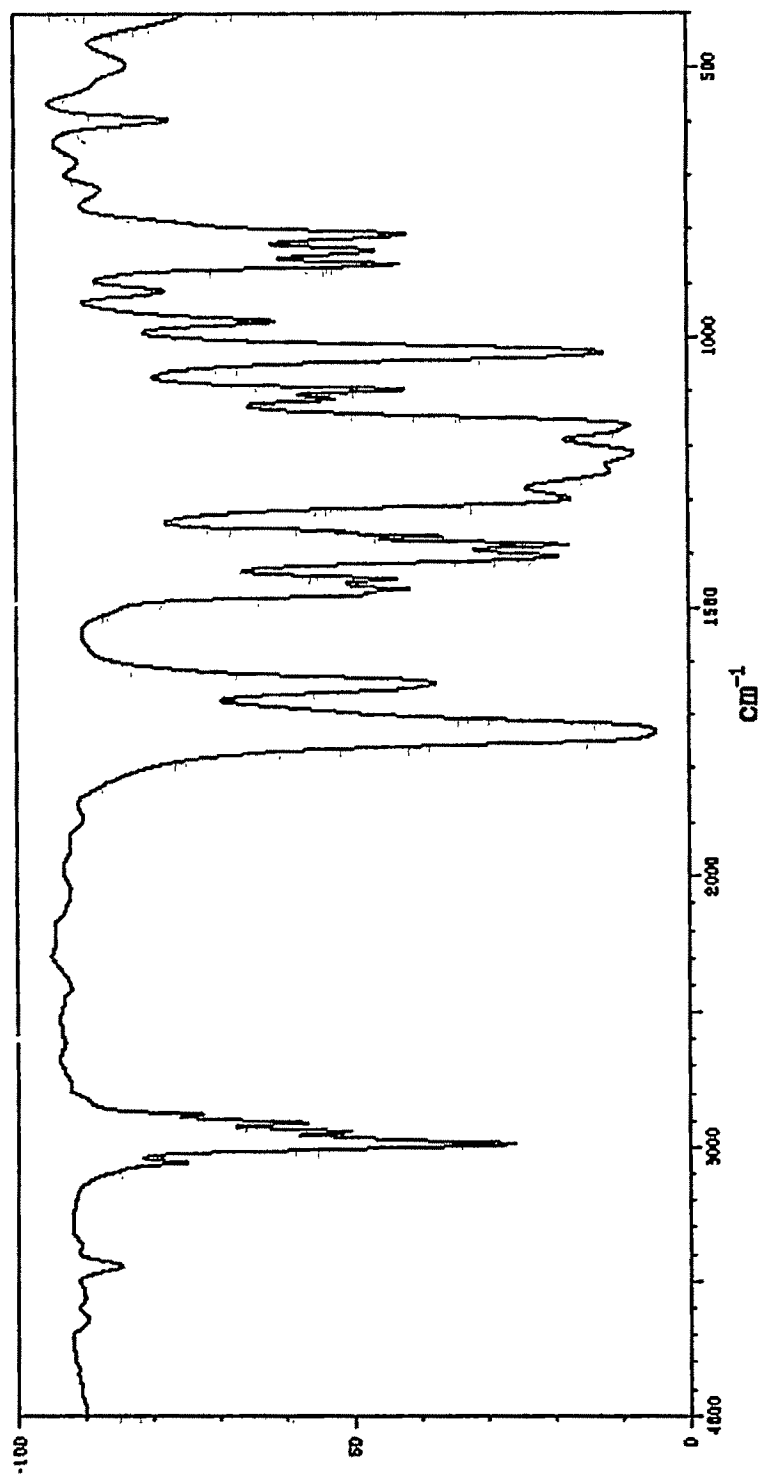
FT-IR (CCl_4) 3050, 2950 (C-H st.), 1750 (C=O st.), 1500(Ar-C=C st), *[1235 (C-O st.), 760 (monosubstituted benzene)] cm^{-1}



****N.B. : Vibrations not included in the syllabus.***

Diethyl Maleate:

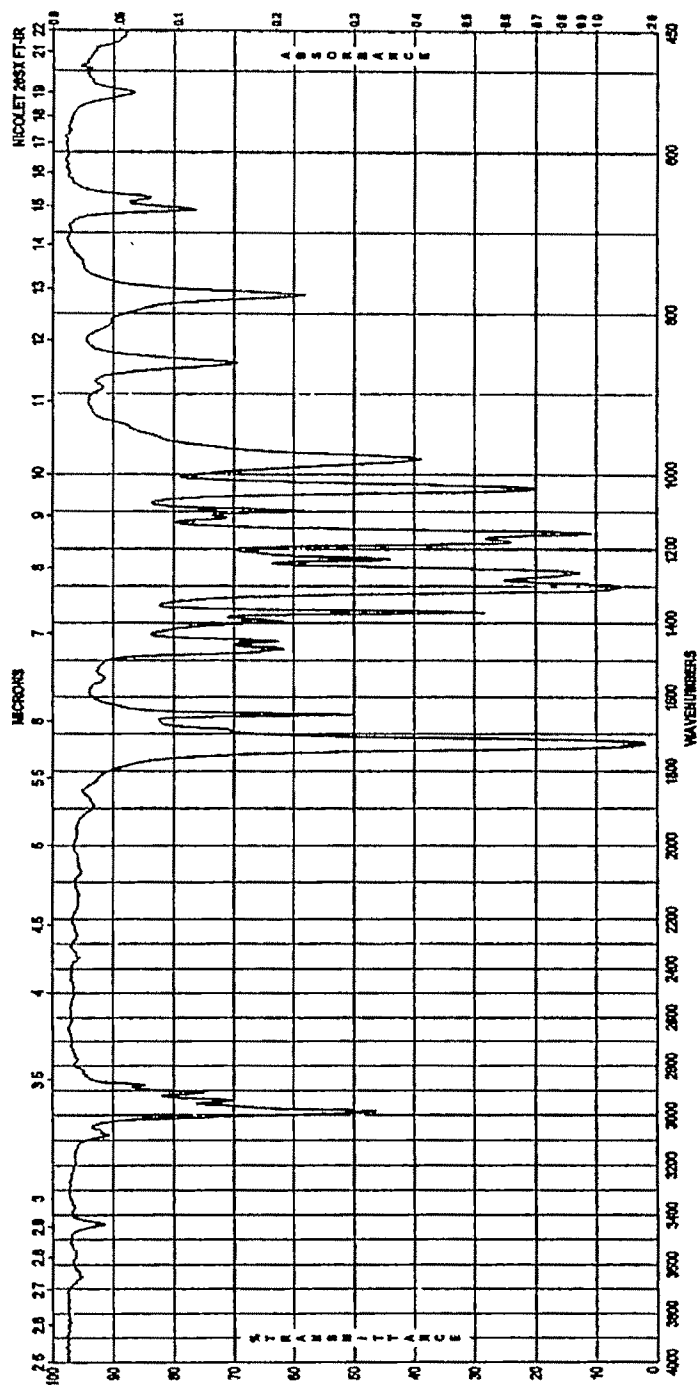
FT-IR (film) 3100-2850(C-H st.), 1730 (C=O st.), 1640 (C=C st.), *[1220 (C-O st.)] cm^{-1} .



*N.B. : Vibration not included in the syllabus.

Diethyl Fumarate:

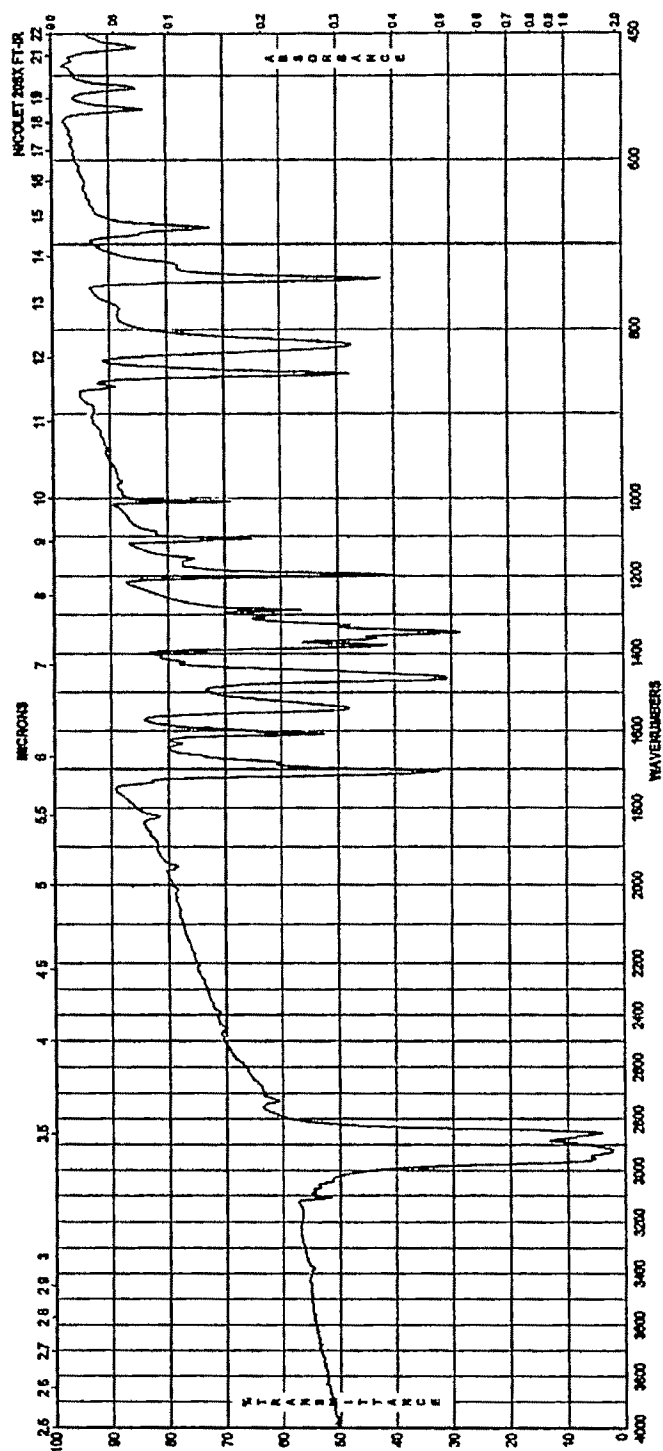
FT-IR (film) 2990-2880 (C-H st.), 1725 (C=O st.), 1650 (C=C st.), *985 (C-H def. *trans* alkene)] cm^{-1} .



*N.B. : Vibration not included in the syllabus.

4-Nitrobenzaldehyde (*p*-Nitrobenzaldehyde):

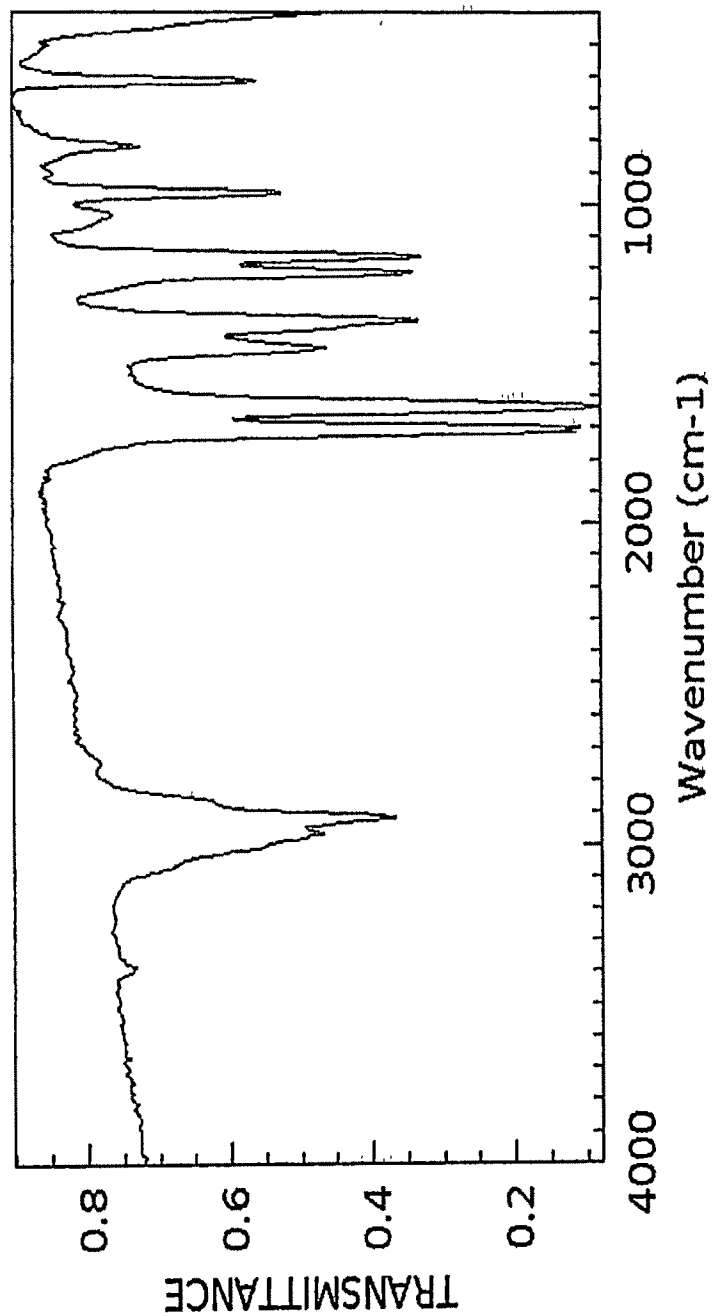
FT-IR (CCl₄) 2970-2900 (C-H st.), 2850, 2730 (C-H st. of -CHO), 1710 (C=O st.), 1600, 1475 (Ar C=C st.) 1540 & 1350 (N=O st. of -NO₂), *[850, 820 (*p*-disubstituted benzene)] cm⁻¹.



*N.B. : Vibrations not included in the syllabus.

Mesityl Oxide:

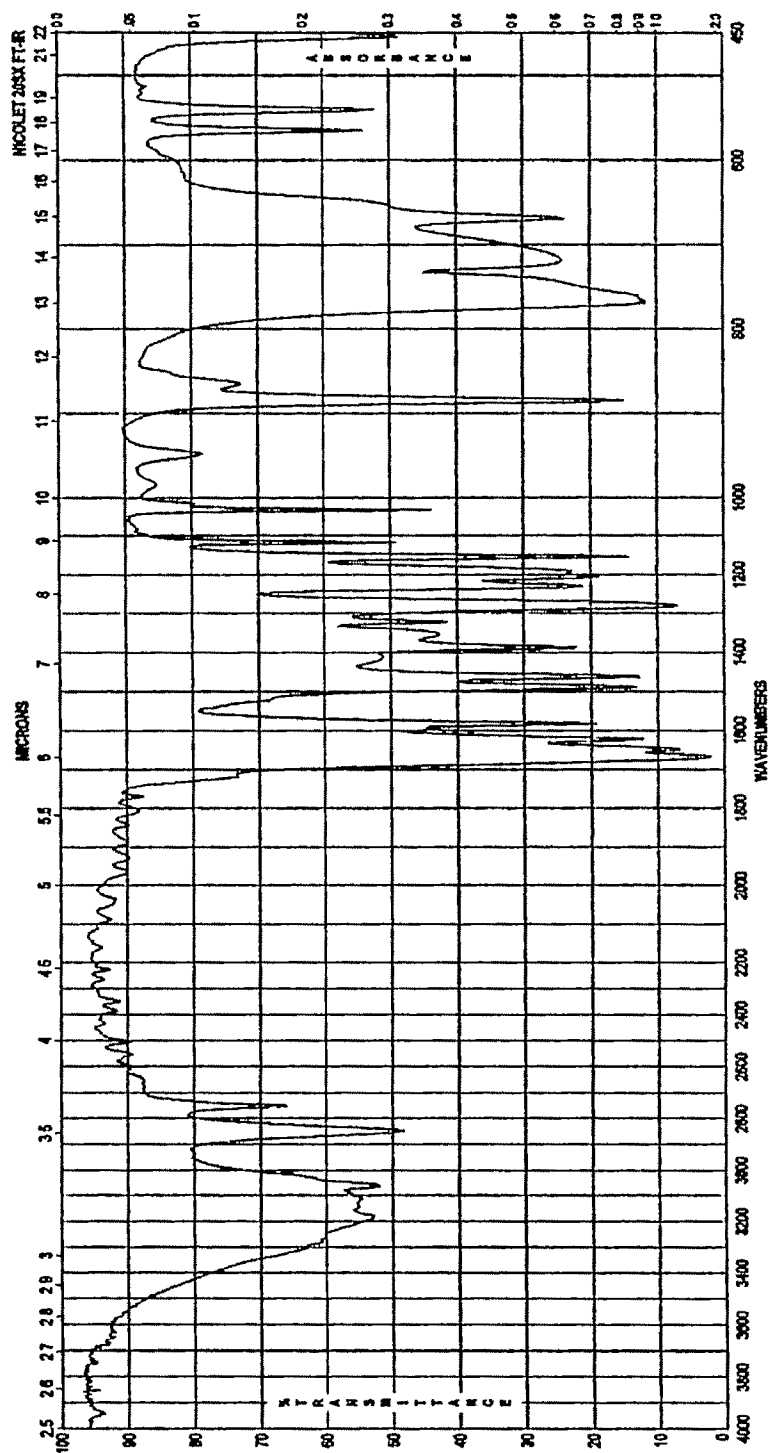
FT-IR (film) 2900 (C-H st.), 1710 (C=O st.), 1640 (C=C st.), *[1450 & 1360 (CMe₂)] cm⁻¹.



*N.B. : Vibrations not included in the syllabus.

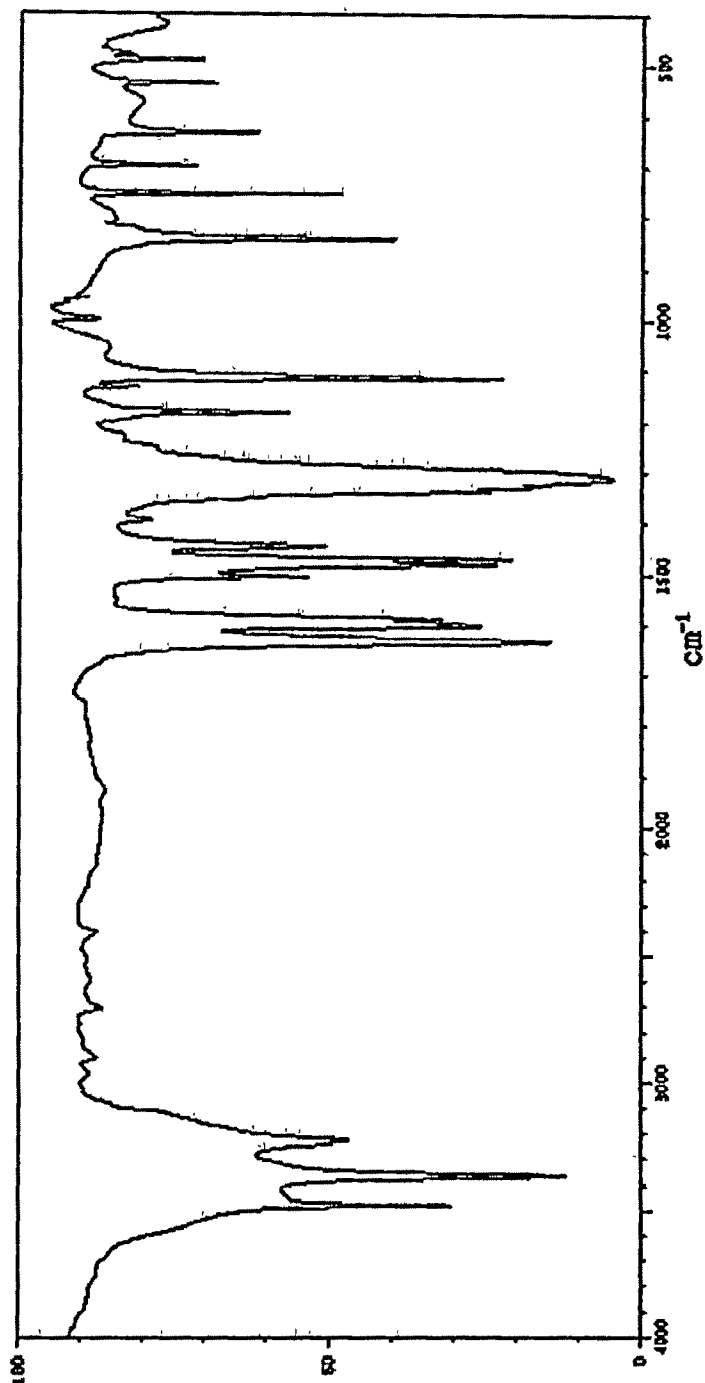
Salicylaldehyde:

FT-IR (film) 3300-3000 (br s, O-H st.), 3060 (C-H st.), 2850, 2750 (C-H st. of -CHO), 1670 (C=O st.) cm^{-1} , 1580, 1490 (Ar-C=C st.).



p-Nitroaniline (4-Nitroaniline):

FT-IR (KBr) 3500 & 3380 (N-H st.), 3200 (sp^2 Ar-C-H st), 1640, 1470 (Ar-C=C st), 1490 & 1320 (N=O st. of -NO₂), *1320 (C-N st.), 840 (*p*-disubstituted benzene) cm^{-1} .



*N.B. : Vibrations not included in the syllabus.

Interpretations of ^1H NMR and IR spectra

**[Vibrations not included in the syllabus.]*

1. ***p*-Bromoacetanilide (4-Bromoacetanilide) :**

^1H NMR (90 MHz, $\text{DMSO}-d_6$) δ 10.0 (br. s, 1H, $-\text{NH}$), 7.54 (d, 2H, ArH) & 7.48 (d, 2H, ArH) 2.05 (s, 3H, CH_3)

FT-IR (CCl_4) 3300 (N-H st.), 2950, 2850 (C-H st. of sp^2 and sp^3 C-H). 1680 (C=O amide I), 1540 (amide II), 1600, 1470 (C=C st. aromatic) cm^{-1} . *[825 *p*-disubstituted benzene, 520 (C-Br st.) cm^{-1}].

2. ***4*-Methyl- α -bromoacetophenone :**

^1H NMR (estimated) δ 7.90 (d, 2H, ArH), 7.17 (d, 2H, ArH), 4.30(s, 2H, CH_2Br), 2.34 (s, 3H, CH_3)

FT-IR (CCl_4) 3050, 2975 (C-H st.), 1710 (C=O st.), 1600 (C=C st. aromatic) cm^{-1} . *[1260 (C-H def), 805 (*p*-disubstituted benzene), 590 (C-Br st.) cm^{-1}].

3. ***Vanillin* :**

^1H NMR (300 MHz, CDCl_3) δ 9.8 (s, 1H, $-\text{CHO}$), 7.35–7.45 (m, 2H), 7.05 (d, 1H), 6.7 (br. s, 1H), 3.85 (s, 3H)

FT-IR (CCl_4) 3550 (O-H st.), 3100-2950 (C-H st. of sp^2 and sp^3 C-H) 2850 & 2750 (C-H st. of $-\text{CHO}$), 1700 (C=O st.) 1600, 1520 (Ar C=C) cm^{-1} . *[1150 (C-O st.) cm^{-1}].

4. ***trans*-Cinnamic acid :**

^1H NMR (300 MHz, CDCl_3) δ 12.7 (br. s, 1H, $-\text{COOH}$), 7.8 (d, 1H, $=\text{CHPh}$), 7.56 (m, 2H, *ortho* Hs), 7.42 (m, 3H, *m*- & *p*-Hs), 6.45 (d, 1H, $=\text{CHCOOH}$)

FT-IR (CCl_4) 3070–2520 (br. O-H st.), 1680 (C=O st.), 1620 (C=C), 1580, 1520 (sp^2 C=C st. aromatic) cm^{-1} . *[990 (C-H def or bending, *trans*-alkene), 760, 710 (C-H o.o.p bending of monosubstituted benzene)]

5. ***p*-Aminobenzoic acid (4-*o*-Aminobenzoic acid) :**

^1H NMR (300 MHz, $\text{CDCl}_3 + \text{DMSO}-d_6$) δ 12.0 (br. s, 1H, $-\text{COOH}$) 7.7 (d, 2H, ArH) & 12.00 br.s, 1H, $-\text{COOH}$), δ 6.6 (d, 2H, ArH) δ 5.9 (br. s, 2H, $-\text{NH}_2$)

FT-IR (CCl_4) 3460 & 3360 (N-H st.), 2930, 2860 (C-H st.), 2700-2500 (O-H st.) 1670 (C=O st.), 1600, 1430 (C=C) cm^{-1} . *[850 (*p*-disubstituted benzene) cm^{-1}].

6. **Salicylamide :**

^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 13.4 (br. s, 1H, $-\text{OH}$), 8.42 & 7.85 (two br. s, 2H, $-\text{NH}_2$), 7.8 (d, 1H, ArH), 7.4 (t, 1H, ArH), 6.75–6.8 (m, 2H, ArH).

FT-IR (CCl_4) 3400 & 3200 (N–H st.), 2900 (C–H st.), 1680 (C=O st.), 1620, 1500 (Ar C=C) 1580 (amide II) cm^{-1} . *[420 (C–N st.), 1250 (C–O st.), 750 (*o*-disubstituted benzene) cm^{-1}].

7. **2-Hydroxyacetophenone (*o*-Hydroxyacetophenone) :**

^1H NMR (300 MHz, CDCl_3 + $\text{DMSO}-d_6$) δ 12.3 (br. s, 1H, $-\text{OH}$), δ 7.84 (d, 1H, ArH), 7.5 (t, 1H, ArH), 6.7–6.9 (m, 2H, ArH), 2.63 (s, 3H, CH_3)

FT-IR (CCl_4) 3200–2850 (br. O–H st.), 3070 (sp^3 C–H st.), 1650 (C=O st.), 1580, 1500 (C=C) cm^{-1} . *[1240 (C–O st.), 760 (*o*-disubstituted benzene) cm^{-1}].

8. **4-Ketopentanoic acid (4-oxopentanoic acid) (Laevulinic Acid) :**

^1H NMR (300 MHz, CDCl_3) δ 10.8 (br.s, 1H, $-\text{COOH}$), 2.7 (t, 2H, CH_2CO), 2.57 (t, 2H, CH_2COOH), 2.2 (s, 3H, CH_3).

FT-IR (CCl_4) 3300–2900 (br. O–H st.), 2700 (C–H st.), 1750 & 1715 (C=O st.) cm^{-1} . *[1430 & 1370 (CH_2 bending) cm^{-1}].

9. **Benzyl Acetate :**

^1H NMR (300 MHz, CDCl_3) δ 7.35 (br. s, 5H, $-\text{Ph}$), 5.1 (s, 2H, $-\text{CH}_2\text{O}-$), 2.1 (s, 3H, $\text{CH}_3\text{COO}-$)

FT-IR (CCl_4) 3050, 2950 (C–H st.), 1750 (C=O st.), 1500 (C=C st., aromatic) cm^{-1} . *[1235 (C–O st.), 760 (monosubstituted benzene) cm^{-1}].

10. **Diethyl Maleate :**

^1H NMR (300 MHz, CDCl_3) δ 6.2 (s, 1H, $-\text{CH=}$), 4.2 (q, 2H, $-\text{CH}_2\text{O}-$), 1.24 (t, 3H, CH_3)

FT-IR (film) 3100–2850 (C–H st.), 1730 (C=O st.), 1640 (C=C st.) cm^{-1} . *[1220 (C–O st.) cm^{-1}].

11. **Diethyl Fumarate :**

^1H NMR (300 MHz, CDCl_3) δ 6.8 (s, 1H, $-\text{CH=}$), 4.19 (q, 2H, $-\text{CH}_2\text{O}-$), 1.30 (t, 3H, CH_3)

FT-IR (film) 2990–2880 (C–H st.), 1725 (C=O st.), 1650 (C=C st.) cm^{-1} . *[985 (C–H def. *trans* alkene) cm^{-1}].

12. **4-Nitrobenzaldehyde (*p*-Nitrobenzaldehyde) :**

^1H NMR (300 MHz, CDCl_3) δ 10.2 (s, 1H, $-\text{CHO}$), 8.42 (d, 2H, *ArH*), 8.14 (d, 2H, *ArH*)
 FT-IR (CCl_4) 2970–2900 (C–H st.), 2850, 2730 (C–H st. of $-\text{CHO}$), 1710 (C=O st.),
 1600, 1475 (sp^2 C=C st. aromatic), 1540 & 1350 (N=O st. of $-\text{NO}_2$) cm^{-1} .
 *[850, 820 (*p*-disubstituted benzene) cm^{-1}].

13. **Mesityl Oxide :**

^1H NMR (300 MHz, CDCl_3) δ 6.08 (s, 1H, $-\text{CH=}$), 2.16 (s, 3H, $\text{CH}_3\text{CO-}$), 2.12 & 1.9
 [2s, 3H each, $(\text{CH}_3)_2\text{C=}$]
 FT-IR (film) 2900 (C–H st.), 1710 (C=O st.), 1640 (C=C st.) cm^{-1} .
 *[1450 & 1360 (CMe_2) cm^{-1}].

14. **Salicylaldehyde :**

^1H NMR (300 MHz, CDCl_3) δ 10.75 (s, $-\text{OH}$), 9.8 (s, 1H, $-\text{CHO}$), 7.5–7.60 (m, 2H,
ArH) 6.95 (m, 2H, *ArH*)
 FT-IR (film) 3300–3000 (br. s, O–H st.), 3060 (C–H st.), 2850, 2750 (C–H st. of $-\text{CHO}$),
 1670 (C=O st.), 1580, 1490 (C=C st.) cm^{-1} .

15. ***p*-Nitroaniline (4-Nitroaniline) :**

^1H NMR (300 MHz, CDCl_3 + $\text{DMSO}-d_6$) δ 7.94 (d, 2H, *ArH*), 6.63 (d, 2H, *ArH*), 6.4
 (br. s, 2H, $-\text{NH}_2$)
 FT-IR (KBr) 3500 & 3380 (N–H st.), 3200 (C–H st.), 1640, 1470 (C=C st.), 1490 & 1320
 (N=O st. of $-\text{NO}_2$, asym. and sym.) cm^{-1} .
 *[1320 (C–N st.), 840 (*p*-disubstituted benzene) cm^{-1}].

Practical Work Book Chemistry (Honours)

Table : Stretching vibrations

Group	Band [position (nature)]	Remarks
Free O-H	3650–3590 (v)	Sharp
H-bonded O-H	3600–3200 (s)	Often broad; the lower the frequency the stronger the H-bond
Chelate type O-H & Carboxylic acid dimers	3200–2500 (v)	Broad; sometimes so broad as to be overlooked
-NH ₂ ; -NH-	3500–3300 (m)	Primary amines show two bands; the unsymmetrical and the symmetrical stretchings.
-CONH ₂	~3500(m) & ~3400(m)	
-CONH-	~3400(m)	
C _{sp} -H	~3300(s)	Sharp
C _{sp2} -H and Aryl-H	3090–3010(m)	Sometimes obscured by stronger bands of saturated C-H
C _{sp3} -H (CH, CH ₂ , CH ₃)	2950–2850(s)	Usually 2 or 3 bands
-CHO	2850–2700(w)	Usually 2 bands
Terminal acetylene (-C≡CH)	2140–2100(w)	ν_{C-H} at 3300 cm ⁻¹
Internal acetylenes (-C≡C-)	2250–2150(v)	weak or absent for nearly symmetrical substitution
Acid anhydrides (-CO-O-CO-) Saturated	~1850(s) & ~1790(s)	Usually separated by ~60 cm ⁻¹ ; the higher frequency asymmetric band is more intense in acyclic anhydrides and the lower frequency symmetric band is more intense in cyclic anhydrides
Acid chlorides (-COCl) Saturated	~1800(s)	

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Group	Band [position (nature)]	Remarks
Esters and lactones ($-\text{CO}-\text{O}-$) Saturated	1750–1735(s)	
Carboxylic acids Saturated	1725–1700	
Aldehydes Saturated	1740–1720(s)	
Ketones Saturated Aryl α , β -Unsaturated 6-ring and larger 5-ring 4-ring	1725–1705(s) 1700–1680(s) 1685–1665(s) Similar to open-chain 1750–1740 ~1780	
Primary amide, $-\text{CONH}_2$ Secondary amide, $-\text{CONH}-$	~1690(s) and ~1600(s) ~1650(s) and ~1640(s) ~1680(s) and ~1530(s)	Solution state: amide I and II Solid state: sometimes overlap; amide I is more intense amide I and II
Isolated $\text{C}=\text{C}$	1680–1620(v)	Weak if more or less symmetrically substituted
Conjugated $\text{C}=\text{C}$	1640–1600(s)	More intense than isolated
Aromatic rings	~1600(m), ~1580(m), ~1500(m)	
$\text{C}-\text{NO}_2$	~1550(s) & ~1380(s)	Asymmetric and symmetric $\text{N}=\text{O}$ st.
$\text{O}-\text{NO}_2$	~1650(s) & ~1300(s)	

Practical Work Book Chemistry (Honours)

Proton NMR chemical shifts (^1H)

Methyl*	δ_{H}	Methyl*	δ_{H}	Olefin H/Alkyne H/Ar H	δ_{H}
R-CH ₃	0.9	N-CH ₃	2.3	C \equiv C-H	2.8
C=C-C-CH ₃	1.1	ArN-CH ₃	3.0	C=CH ₂	5.6
O-C-CH ₃	1.3	RCON-CH ₃	2.9	HC(OR)=CH ₂	4.1
C=C-CH ₃	1.6	RO-CH ₃	3.3	HC(OR)=CH ₂	6.5
C \equiv C-CH ₃	1.8	RCOO-CH ₃	3.7	RCOCH=CH ₂	6.2
RCO-CH ₃	2.1	ArO-CH ₃	3.8	RCOCH=CH ₂	6.4
ROCO-CH ₃	2.2	C=C-O-CH ₃	3.8	Ph-H	7.27
Ar-CH ₃	2.3			Nitrobenzene <i>ortho</i> H	8.15
				<i>meta</i> H	8.5
				<i>para</i> H	8.65
ArOOC-CH ₃	2.4	F-CH ₃	4.3	Benzaldehyde <i>ortho</i> H	7.8
				<i>meta</i> H	7.5
				<i>para</i> H	7.6
ArOC-CH ₃	2.6	Cl-CH ₃	3.1	Anisole <i>ortho</i> H	6.8
				<i>meta</i> H	7.18
				<i>para</i> H	6.85
cyclopropane	0.3	Br-CH ₃	2.7	Aniline <i>ortho</i> H	6.55
				<i>meta</i> H	7.0
				<i>para</i> H	6.6
cyclobutane	1.96	I-CH ₃	2.1	Benzoic acid <i>ortho</i> H	8.1
				<i>meta</i> H	8.45
				<i>para</i> H	8.55
cyclohexane	1.44	RS-CH ₃	2.1	Bromobenzene <i>ortho</i> H	7.4
				<i>meta</i> H	7.2
				<i>para</i> H	7.2

*Chemical shift (δ_{H}) of methylene and methine Hs will increase by ~0.4 and ~0.6 respectively.

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Format for Recording of FT-IR and ^1H NMR Data in Laboratory Notebook

A. Infrared spectrum of _____

Spectrum recorded in solid state/ solution (solvent)/ liquid state

Stretching Vibrations (in cm^{-1})	Nature	Probable Assignment

B. ^1H NMR spectrum of _____

Spectrum recorded in _____ MHz instrument in solvent using TMS as internal standard

Chemical Shift δ (in ppm)	Splitting Pattern	Relative Ratio of Hs	Probable Assignment

***N.B.:** Detailed description of the spectra of known organic compounds are given later

Examples

Infrared Spectrum of *p*-Bromoacetanilide

Spectrum recorded in solution using CCl_4 solvent

Stretching Vibrations (in cm^{-1})	Nature Probable	Assignment
3300	m	N-H stretching of amide
2950, 2850	s	C-H stretching
1680	s	C=O stretching (amide I)
1600, 1470	s	Aromatic C=C stretching
1540	s	N-H bending (amide II)

^1H NMR Spectrum of *trans*-Cinnamic Acid

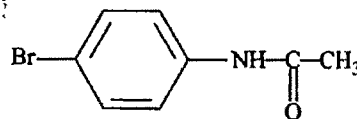
Spectrum recorded in 300 MHz instrument in CDCl_3 using TMS as internal standard

Chemical Shift δ (in ppm)	Splitting Pattern	Relative Ratio of Hs	Probable Assignment
12.7	br. s	1	$-\text{COOH}$
7.8	d	1	$-\text{HC}=\text{CCOOH}$
7.56	m	2	<i>ortho</i> ArH
7.42	m	3	other ArH
6.45	d	1	$-\text{C}=\text{CHCOOH}$

FT-IR ANALYSIS OF ORGANIC COMPOUNDS

Assignment of labelled peaks of known organic compounds C-H, O-H, N-H, C=C, C=O, (*Vibrations are not included in the syllabus) NO₂ stretching frequencies) in FT-IR.

1. *p*-Bromoacetanilide (4-Bromoacetanilide)

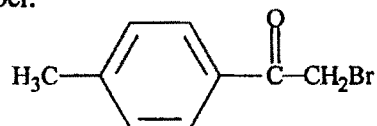


Spectrum recorded in solution using CCl₄ solvent.

	Stretching Vibration (cm ⁻¹)	Nature	Probable Assignment
(a)	3300	m	N-H stretching frequency of amide
(b)	2950, 2850	s	C-H stretching frequencies of sp ² C-H and sp ³ C-H overlap
(c)	1680	s	C=O stretching (amide I) frequency
(d)	1600, 1470	s	C=C stretching frequency for aromatic ring
(e)	1540	s	N-H bending (amide II) frequency

- The N-H stretching frequency of *p*-bromoacetanilide appears at normal N-H stretching region at 3300 cm⁻¹.
- The C-H stretching frequency appears in the region 2950 and 2850 cm⁻¹ where sp² (aromatic) C-H stretching overlaps with sp³ C-H stretching.
- A strong C=O stretching band comes at 1680 cm⁻¹ for amide I.
- The C=C stretching for aromatic ring appears in the region 1600 and 1470 cm⁻¹.
- At 1540 cm⁻¹ N-H bending frequency appears (amide II) which has much lower stretching frequency compared to N-H stretching as bending requires less energy than stretching and hence corresponds to lower wave number.

2. 4-Methyl- α -bromoacetophenone



Spectrum recorded in solution using CCl₄ solvent.

	Stretching Vibration (cm ⁻¹)	Nature	Probable Assignment
(a)	3050	w	C-H stretching frequency (aryl sp ² C-H stretching)
(b)	2975	w	C-H stretching frequency (sp ³ C-H stretching)
(c)	1710	s	C=O stretching frequency conjugated
(d)	1600	m	C=C stretching frequency for the aromatic ring

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	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
*(e)	1260	s	C-H bending frequency of C-Me
*(f)	805	w	C-H out of plane (o.o.p) bending frequency of <i>p</i> -disubstituted benzene ring
*(g)	590	w	C-Br stretching frequency

(a) and (b) : C-H stretching (a) is of higher frequency than that of (b). In C-H (a), the carbon atom is sp^2 hybridised whereas in C-H (b), the carbon atom is sp^3 hybridised. sp^2 hybridised carbon is more electronegative than sp^3 hybridised carbon as the former bears more s character. So the electronegativity difference between C and H in sp^2 C-H bond is more. Now, higher is the difference in electronegativity between C and H, higher is the strength of C-H bond and higher will be the force constant. As a result, sp^2 C-H stretching frequency will be higher than sp^3 C-H stretching frequency.

(c) The C=O stretching of 4-methyl- α -bromoacetophenone is lower (1710 cm^{-1}) than normal C=O stretching frequency ($\sim 1720 \text{ cm}^{-1}$) because of conjugation with the benzene ring.

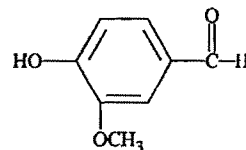
(d) C=C stretching frequency appears at 1600 cm^{-1} which is aromatic sp^2 C=C stretching frequency.

*(e) C-H bending frequency of C-Me appears at 1260 cm^{-1} .

*(f) C-H o.o.p bending frequency of *p*-disubstituted benzene ring comes at 805 cm^{-1} .

*(g) C-O stretching frequency comes at 1150 cm^{-1} .

3. Vanillin



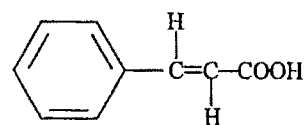
Spectrum recorded in solution using CCl_4 solvent.

	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(a)	3550	s	O-H stretching frequency (no intermolecular hydrogen bond present).
(b)	3100-2950	w	sp^2 C-H stretching and sp^3 C-H stretching frequencies overlap each other.
(c)	2850, 2750 (Fermi Resonance)	w	Coupled C-H stretching frequency of aldehyde (-CHO) (doublet due to Fermi resonance).
(d)	1700	s	C=O stretching frequency.
(e)	1600, 1520	s	C=C stretching frequency for aromatic ring.
*(f)	1150	s	C-O stretching frequency.

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- (a) O–H stretching frequency gives a sharp signal as there can be no intermolecular hydrogen bonding between the solvent (CCl_4) and the sample (vanillin).
- (b) sp^2 C–H stretching and sp^3 C–H stretching frequencies overlap in the region $3100\text{--}2950\text{ cm}^{-1}$.
- (c) 2850 and 2750 cm^{-1} frequencies stand for C–H stretching of aldehyde coupled with C–H stretching of sp^3 C–H bonds. This doublet is a result of **Fermi resonance**.
- (d) Normal aldehyde signal comes at 1700 cm^{-1} which is a strong peak.
- (e) 1600 and 1520 cm^{-1} are frequencies for aromatic sp^2 C=C stretching.
- *(f)** C–O stretching frequency comes at 1150 cm^{-1} .

4. *trans*-Cinnamic Acid



Spectrum recorded in solution using CCl_4 solvent.

	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(a)	3070–2520	br. s	Broad O–H stretching frequency is due to intermolecular hydrogen bonding.
(b)	3000	s	Aromatic sp^2 C–H stretching frequency.
(c)	1680	s	C=O stretching frequency, conjugated.
(d)	1620, 1430	s	C=C stretching frequency, conjugated.
(e)	1580, 1520	m	Aromatic sp^2 C=C stretching frequency.
*(f)	990	s	C–H o.o.p bending frequency of <i>trans</i> -alkene.
*(g)	760, 710	m	C–H o.o.p bending frequency of monosubstituted benzene molecule.

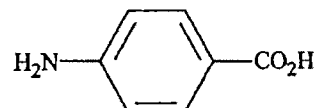
- (a) A broad signal for O–H stretching ($3070\text{--}2520\text{ cm}^{-1}$) comes due to intermolecular hydrogen bonding. Lengthening of the original O–H bond occurs, hence force constant decreases. As a result, O–H stretching needs lesser amount of energy and the stretching frequency gets lowered.
- (b) Aromatic sp^2 C–H stretching frequency comes at 3000 cm^{-1} .
- (c) C=O stretching frequency is lowered (1680 cm^{-1}) due to extended conjugation and intermolecular hydrogen bond formation. C=O bond gets partial single bond character and hence the force constant of C=O bond decreases. So, for C=O stretching, lesser amount of energy is required which results in lowering of stretching frequency.
- (d) C=C stretching frequency is also lowered due to conjugation (1620 cm^{-1}).
- (e) 1580 and 1520 cm^{-1} stand for stretching frequencies of aromatic sp^2 C=C bond.

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***(f)** C–H o.o.p bending frequency of *trans*-alkene comes at 990 cm⁻¹.

***(g)** C–H o.o.p bending frequencies appear at 760 and 710 cm⁻¹.

5. *p*-Aminobenzoic Acid (4-Aminobenzoic Acid)



Spectrum recorded in solution using CCl₄ solvent.

	Stretching Vibration (cm ⁻¹)	Nature	Probable Assignment
(a)	3460	m	N–H stretching (asymmetric) frequency.
(b)	3360	m	N–H stretching (symmetric) frequency.
(c)	2930, 2860	s	aromatic sp ² C–H stretching frequency.
(d)	2700–2500	w	O–H stretching frequency.
(d)	1670	m	C=O stretching frequency, conjugated.
(e)	1600, 1430	m	aromatic C=C stretching frequency.

(a) **Asymmetric** N–H stretching frequency appears at higher frequency as it has higher force constant.

(b) **Symmetric** N–H stretching frequency appears at lower frequency due to lower force constant.

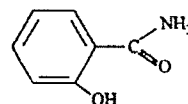
(c) Aromatic sp² C–H stretching frequencies appear at 2930 and 2860 cm⁻¹.

(d) O–H stretching frequency shows lower value (2700–2500 cm⁻¹) and broad nature due to **intermolecular** hydrogen bonding.

(e) Acid C=O stretching frequency appears at 1670 cm⁻¹ which experiences extended conjugation.

(f) Aromatic sp² C=C stretching frequencies appear at 1600 and 1430 cm⁻¹.

6. Salicylamide



Spectrum recorded in solution using CCl₄ solvent.

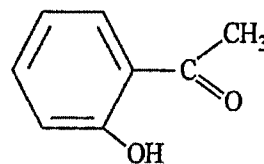
	Stretching Vibration (cm ⁻¹)	Nature	Probable Assignment
(a)	3400	s	N–H stretching frequency (asymmetric) overlaps with O–H stretching frequency (no intermolecular hydrogen bonding).
(b)	3200	s	N–H stretching (symmetric) frequency.
(c)	2900	s	aromatic sp ² C–H stretching frequency.
(d)	1680	s	C=O stretching frequency, conjugated (amide I).

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	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(e)	1620, 1500	s	aromatic $\text{C}=\text{C}$ stretching ($\text{sp}^2 \text{C}=\text{C}$) frequency.
(f)	1580	s	N-H bending (amide II) frequency.
*(g)	1420	s	C-N stretching.
*(h)	1250	s	C-O stretching frequency of Ar-OH/C-H bending frequency.
*(i)	750	s	<i>o</i> -disubstituted benzene molecule.

- (a) 3400 cm^{-1} stands for N-H **asymmetric** stretching frequency which vibrates at a higher frequency, overlaps with O-H stretching frequency. The signal for O-H stretching frequency is sharp as there is no possibility of intermolecular hydrogen bonding with the solvent taken (CCl_4).
- (b) 3200 cm^{-1} stands for N-H **symmetric** stretching frequency which vibrates at a lower frequency.
- (c) $\text{sp}^2 \text{C-H}$ (aromatic) stretching frequency appears at 2900 cm^{-1} .
- (d) $\text{C}=\text{O}$ stretching for **amide I** comes at 1680 cm^{-1} which has lower value due to conjugation with the lone pair of electrons on N atom.
- (e) Aromatic $\text{sp}^2 \text{C}=\text{C}$ stretching frequencies appear at 1620 and 1500 cm^{-1} .
- (f) N-H bending (**amide II**) appears at 1580 cm^{-1} . As bending requires less energy, the lowering of frequency occurs compared to stretching one.
- *(g) C-N stretching frequency appears at 1420 cm^{-1} .
- *(h) Due to resonance, the C-O bond gets partial double bond character and as a result, force constant of C-O bond increases and stretching frequency of C-O bond increases.
- *(i) C-H out of plane bending frequency for *o*-disubstituted benzene molecule comes at 750 cm^{-1} .

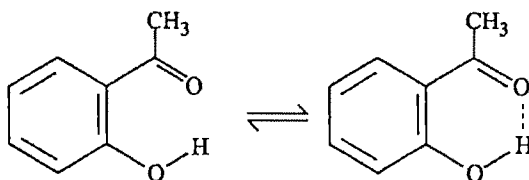
7. 2-Hydroxyacetophenone



Spectrum recorded in solution using CCl_4 solvent.

	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(a)	3200-2850	Broad (br)	O-H stretching frequency (intramolecularly hydrogen bonded).
(b)			$\text{sp}^2 \text{C-H}$ stretching frequency.

	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(c)	1650	s	C=O stretching frequency (conjugated as well as intramolecularly hydrogen bonded).
(d)	1580, 1500	m	aromatic sp^2 C=C stretching frequency.
*(e)	1240	s	C-H stretching frequency.
*(f)	760	s	C-H bending frequency.



- (a) 3200–2750 range gives a broad signal for O–H stretching frequency. O–H group is

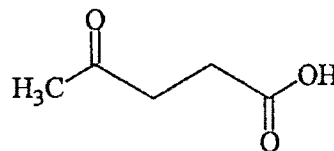
$$\begin{array}{c} \text{O} \\ || \\ \text{Ar}-\text{C}-\text{CH}_3 \end{array}$$

intramolecularly hydrogen bonded with C=O group of $\text{Ar}-\text{C}-\text{CH}_3$. As a result, lengthening of the original O–H bond occurs and force constant of O–H bond decreases. So less amount of energy is required for stretching of O–H bond which results in lowering of stretching frequency.

- (b) sp^2 C–H stretching frequency comes at 3070 cm^{-1} .
- (c) C=O stretching frequency comes at 1650 cm^{-1} . Due to **intramolecular** hydrogen bonding and extended conjugation, C=O bond, bears a partial single bond character. So, force constant of C=O bond decreases and C=O bond stretching thus needs lesser amount of energy. It results in lowering of C=O stretching frequency.
- (d) 1580 and 1500 cm^{-1} signals stand for aromatic sp^2 C=C stretching frequency.
- *(e) Due to resonance, C–O bond gets partial double bond character and as a result, force constant of C–O bond increases and stretching frequency of C–O bond increases.
- *(f) C–H o.o.p bending frequency of *o*-disubstituted benzene molecule comes at 760 cm^{-1} .

8. 4-Ketopentanoic Acid

(4-Oxopentanoic Acid or Laevulinic Acid)



Spectrum recorded in solution using CCl_4 solvent.

	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(a)	3300–2900	Broad (br)	O–H stretching frequency (intramolecularly hydrogen bonded) frequency.

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	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(b)	2700	m	C-H stretching frequency.
(c)	1750	s	C=O stretching frequency of $\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{OH} \end{array}$ group.
(d)	1715	s	C=O stretching frequency of keto carbonyl $\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{C}- \end{array}$ group.

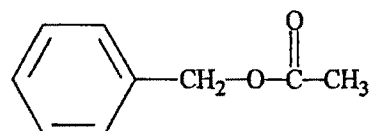
(a) 4-ketopentanoic acid shows broad O-H signal at $3300\text{--}2900\text{ cm}^{-1}$ as the acid forms a **dimer** by strong intermolecular hydrogen bonding. O-H stretching frequency gets lowered from the original value as lengthening of the bond takes place and force constant of O-H bond decreases.

(b) Stretching frequency at 2700 cm^{-1} corresponds to sp^3 C-H bonds.

(c) The C=O group of a carboxylic acid group ($\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{OH} \end{array}$) shows higher value compared to the stretching frequency of a keto carbonyl group. So signal at 1750 cm^{-1} corresponds to stretching frequency of C=O of -COOH group of 4-ketopentanoic acid, due to its higher force constant.

(d) C=O stretching frequency of keto carbonyl group of 4-ketopentanoic acid appears at 1715 cm^{-1} which has lower wave number than that of C=O of -COOH group, as it has a lower force constant.

9. Benzyl Acetate



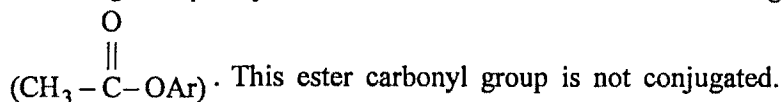
Spectrum recorded in solution using CCl_4 solvent.

	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(a)	3050, 2950	m	C-H stretching frequency for sp^2 C-H and sp^3 C-H overlap each other.
(b)	1750	s	C=O stretching frequency of $\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{OAr} \end{array}$ moiety (not conjugated).
(c)	1500	m	aromatic sp^2 C=C stretching frequency.

(a) Higher frequency region (3050 cm^{-1}) corresponds to the stretching frequency of sp^2 C-H bonds and the lower frequency region (2950 cm^{-1}) corresponds to the stretching frequency of sp^3 C-H bonds.

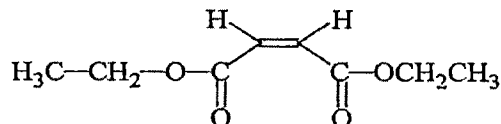
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- (b) Stretching frequency at 1750 cm^{-1} stands for $\text{C}=\text{O}$ signal of acetate ester



- (c) Aromatic $\text{sp}^2\text{ C}=\text{C}$ stretching frequency appears at a lower frequency (1500 cm^{-1}) compared to $\text{sp}^2\text{ C}=\text{C}$ stretching frequency that is not aromatic.

10. Diethyl Maleate

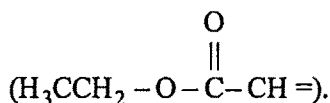


Spectrum recorded in liquid state as thin film.

	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(a)	3100–2850	m	$\text{sp}^3\text{ C-H}$ stretching frequency.
(b)	1730	s	$\text{C}=\text{O}$ stretching frequency of ester carbonyl $\begin{array}{c} \text{O} \\ \\ (= \text{CH} - \text{C} - \text{OCH}_2\text{CH}_3) \end{array}$ group.
(c)	1640	m	$\text{sp}^2\text{ C}=\text{C}$ stretching frequency (not aromatic) $\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \end{array}$ moiety).

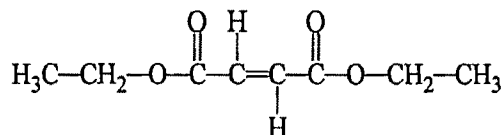
- (a) Stretching frequency in the region $3100\text{--}2850\text{ cm}^{-1}$ stands for $\text{sp}^3\text{ C-H}$ bonds.

- (b) At 1730 cm^{-1} , the stretching frequency corresponds to ester carbonyl group



- (c) At 1640 cm^{-1} , the stretching frequency corresponds to $\text{sp}^2\text{ C}=\text{C}$ which is **not aromatic** and comes at a comparatively higher frequency with respect to aromatic $\text{sp}^2\text{ C}=\text{C}$ stretching frequency.

11. Diethyl Fumarate



Spectrum recorded in liquid state as thin film.

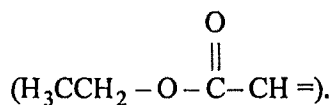
	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(a)	2990–2880	m	$\text{sp}^3\text{ C-H}$ stretching frequency.
(b)	1725	s	Stretching frequency of $\text{C}=\text{O}$ of ester.

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	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(c)	1650	m	$\begin{array}{c} \text{O} \\ \\ \text{CH} - \text{C} - \text{OCH}_2\text{CH}_3 \end{array}$ carbonyl group. $\text{sp}^2 \text{C}=\text{C}$ stretching frequency (not aromatic) $\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \end{array}$ moiety) .

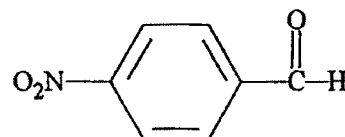
(a) Stretching frequency in the region $2990\text{--}2880 \text{ cm}^{-1}$ stands for $\text{sp}^3 \text{C-H}$ bonds.

(b) At 1725 cm^{-1} , the stretching frequency corresponds to ester carbonyl group



(c) At 1650 cm^{-1} , the stretching frequency corresponds to $\text{sp}^2 \text{C}=\text{C}$ which is **not aromatic** and comes at a comparatively higher frequency with respect to aromatic $\text{sp}^2 \text{C}=\text{C}$ stretching frequency.

12. 4-Nitrobenzaldehyde, (*p*-Nitrobenzaldehyde)



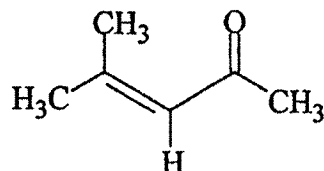
Spectrum recorded in solution using CCl_4 solvent.

	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(a)	2970–2900	s	aromatic $\text{sp}^2 \text{C-H}$ stretching
(b)	2850, 2730 (Fermi Resonance)	s	C-H doublet stretching frequencies of $-\text{CHO}$ group due to Fermi resonance for an aldehyde moiety.
(c)	1710	s	$\begin{array}{c} \text{O} \\ \\ -\text{C} - \text{H} \end{array}$ C=O stretching frequency of $-\text{C}-\text{H}$ group. (undergoing conjugation with the benzene ring).
(d)	1600, 1475	m	aromatic $\text{sp}^2 \text{C}=\text{C}$ stretching frequency.
(e)	1540, 1350	m	asymmetric and symmetric stretching frequencies of N=O bond of $-\text{NO}_2$ group respectively.
*(f)	850, 820	m	C-H o.o.p bending frequency of <i>p</i> -disubstituted benzene ring.

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- (a) The region 2970–2900 cm^{-1} indicates the stretching frequency of aromatic sp^2 C–H bonds.
- (b) The stretching frequencies at 2850 and 2730 cm^{-1} correspond to the C–H stretching frequencies of $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{H} \end{array}$ group as a **doublet** due to **Fermi resonance** in an aldehyde.
- (c) Resonance weakens C=O bond resulting in absorption at a lower frequency as lesser amount of energy is required for C=O bond stretching.
- (d) Aromatic sp^2 C=C stretching frequency appears at 1620 cm^{-1} .
- (e) **Asymmetric** stretching frequency of N=O bond of $-\text{NO}_2$ group comes at 1540 cm^{-1} whereas **symmetric** stretching frequency of N=O bond of $-\text{NO}_2$ group appears at 1350 cm^{-1} . It needs more energy to stretch the N=O bond asymmetrically compared to stretch the same bond symmetrically. So N=O asymmetric stretching frequency is higher (1540 cm^{-1}) compared to the N=O symmetric stretching frequency (1350 cm^{-1}).
- *(f) C–H out of plane bending frequencies of *p*-disubstituted benzene molecule come at 850 and 820 cm^{-1} .

13. Mesityl Oxide

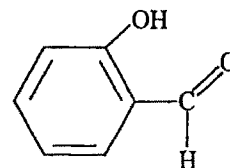


Spectrum recorded in liquid state as thin film.

	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(a)	2900	m	sp^3 C–H stretching frequency.
(b)	1710	s	C=O stretching frequency of keto carbonyl group, conjugated.
(c)	1640	s	sp^2 C=C stretching frequency, conjugated but not aromatic.

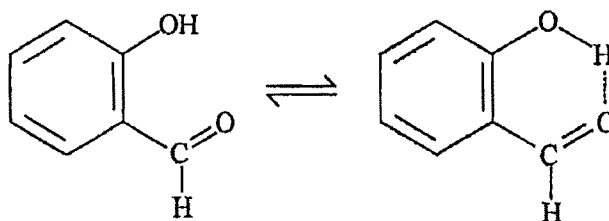
- (a) sp^3 C–H stretching frequency comes at 2900 cm^{-1} .
- (b) C=O stretching frequency of keto carbonyl group appears at 1710 cm^{-1} . Conjugation weakens C=O bond resulting in absorption at a lower frequency as lesser amount of energy is required for C=O bond stretching.
- (c) 1640 cm^{-1} is the stretching frequency for conjugated C=C bond which is not aromatic in nature.

14. Salicylaldehyde

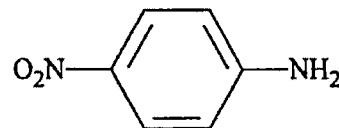


Spectrum recorded in liquid state as thin film.

	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(a)	3300–3000	Broad hump(br)	O–H stretching frequency (intramolecularly hydrogen bonded)
(b)	3060	m	sp^2 C–H stretching frequency (aromatic)
(c)	2850, 2750 (Fermi Resonance)	m	C–H doublet frequencies of –CHO indicates Fermi Resonance for an aldehyde moiety.
(d)	1670	s	C=O stretching frequency of –CHO group.
(e)	1580, 1490	s	aromatic sp^2 C=C stretching frequency



- (a) A broad hump comes in the region $3300\text{--}3000\text{ cm}^{-1}$ due to O–H stretching. Due to **intramolecular hydrogen bonding**, lengthening of the original O–H bond occurs and force constant of O–H bond decreases. Thus for O–H bond stretching, lesser amount of energy is required and lowering of stretching frequency occurs. Intramolecular hydrogen bonding occurs between C=O group of aldehyde and phenolic OH group.
- (b) Aromatic sp^2 C–H stretching frequency appears at 3060 cm^{-1} .
- (c) The stretching frequencies at 2850 and 2750 cm^{-1} correspond to the C–H stretching frequencies of --C=O group comes as a doublet due to **Fermi resonance** in an aldehyde.
- (d) C=O stretching frequency appears at 1670 cm^{-1} . Intramolecular hydrogen bonding and extended conjugation weaken C=O bond resulting in absorption at a lower frequency value as lesser amount of energy is required for C=O stretching.
- (e) Aromatic sp^2 C=C stretching comes at 1580 and 1490 cm^{-1} .

15. *p*-Nitroaniline (4-Nitroaniline)

Spectrum recorded in solid state forming pellet with solid KBr.

	Stretching Vibration (cm^{-1})	Nature	Probable Assignment
(a)	3500, 3380	m,s	N-H symmetric and asymmetric stretching frequencies respectively.
(b)	3200	m	aromatic sp^2 C-H stretching frequency.
(c)	1640, 1470	s,s	aromatic sp^2 C=C stretching frequencies.
(d)	1490, 1320	s,s	asymmetric and symmetric stretching frequencies of N=O of $-\text{NO}_2$ group.
*(e)	1320	s	C-N stretching frequency.
*(f)	840	m	C-H o.o.p bending frequency of <i>p</i> -disubstituted benzene ring.

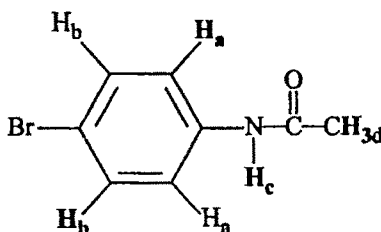
- (a) The stretching frequencies at 3500 and 3380 cm^{-1} correspond to N-H **asymmetric** and **symmetric** stretching frequencies of $-\text{NH}_2$ group respectively. Asymmetric N-H stretching frequency comes at a higher frequency compared to that of symmetric N-H stretching frequency because in the former case more energy is needed to stretch N-H bond asymmetrically.
- (b) At 3200 cm^{-1} aromatic sp^2 C-H stretching frequency appears.
- (c) At frequencies 1640 and 1470 cm^{-1} aromatic sp^2 C=C stretching frequency appears.
- (d) **Asymmetric** stretching frequency of N=O bond of $-\text{NO}_2$ group comes at 1490 cm^{-1} , **symmetric** stretching frequency of N=O bond of NO_2 group appears at 1320 cm^{-1} . It needs more energy to stretch the N=O bond asymmetrically compared to stretch the same bond symmetrically. So, N=O asymmetric stretching frequency becomes higher (1490 cm^{-1}) compared to N=O symmetric stretching frequency (1320 cm^{-1}).
- *(e) C-N stretching frequency comes at 1320 cm^{-1} .
- *(f) C-H out of plane bending frequency, a characteristic of *p*-disubstituted benzene molecule comes at 840 cm^{-1} .

PMR ANALYSIS OF ORGANIC COMPOUNDS

Assignment of labelled peaks in the ^1H NMR spectrum of known organic compounds, explaining the relative δ values and splitting pattern.

1. ^1H NMR Spectrum of *p*-Bromoacetanilide (4-Bromoacetanilide)

Spectrum was recorded in 89.56 MHz instrument in $\text{DMSO}-d_6$ solvent using TMS as internal standard.



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	10.0	br. s	1	H_c proton (Amide proton of $\text{Ar}-\text{N}-\text{COCH}_3$) H_c
(b)	7.54	d	2	H_a protons (aromatic)
(b)	7.48	d	2	H_b protons (aromatic)
(c)	2.05	s	3	H_d protons (Acetyl protons of $\text{ArNH}-\text{C}(=\text{O})-\text{CH}_3$)

- (a) $\delta = 10.0$ is assigned to amide proton (H_c proton of $\text{Ar}-\text{N}-\text{COCH}_3$). H_c appears as



a broad singlet (br, s) due to intermolecular hydrogen bond between $\text{C}=\text{O}$ and $-\text{NH}$ moieties.

- (b) $\delta = 7.54$ is assigned to two aromatic H_a protons which are *ortho* to $-\text{NHCOCH}_3$ group. H_a protons give rise to (2H, d) (two proton, doublet) signal. Two H_a protons are more deshielded ($d = 7.54$) than two H_b protons ($d = 7.48$) since NHCOCH_3 group is more electron withdrawing than Br.

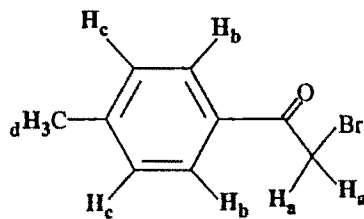
(b') $\delta = 7.48$ is assigned to two aromatic H_b protons which are *ortho* to Br and they give rise to (2H, d) (two proton, doublet) signal.

H_a and H_b protons represent a complex AA' BB' system of *p*-disubstituted benzene derivative where substituents are different; so H_a and H_b appear as a pair of doublets.

(c) $\delta = 2.05$ is assigned to H_d protons of $Ar-NH-\overset{\overset{O}{||}}{C}-CH_{3d}$. They appear as (3H, s) (three proton, singlet). The peak appears as a singlet as there is no adjacent hydrogen to couple with.

2. 1H NMR Spectrum of 4-Methyl- α -bromoacetophenone

The spectrum was recorded in 300 MHz instrument in $CDCl_3$ solvent using TMS as internal standard.



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	7.90	d	2	H_b protons (aromatic)
(b)	7.17	d	2	H_c protons (aromatic)
(c)	4.30	s	2	H_a protons of $Ar-\overset{\overset{O}{ }}{C}-CH_{2a}Br$
(d)	2.34	s	3	H_d protons of $BrCH_2-\overset{\overset{O}{ }}{C}-C_6H_4-CH_{3d}$

(a) $\delta = 7.90$ is assigned to two aromatic H_b protons which are *ortho* to $-\overset{\overset{O}{||}}{C}-CH_2Br$ group.

These two protons are maximum deshielded due to diamagnetic anisotropy of the $C=O$ group and also by the (-I) effect of carbonyl group. H_b protons appear as (two proton, doublet) (2H, d) as they couple with *ortho* H_c protons. (*ortho* coupling).

(b) $\delta = 7.17$ is assigned to two aromatic H_c protons which are present *ortho* to $-CH_3$ and

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meta to $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{CH}_2\text{Br} \end{array}$ group. These protons are less deshielded compared to H_b protons

as they do not fall in the deshielding zone of $\text{C}=\text{O}$ group. H_c proton appear as (two proton, doublet) (2H, d) as they couple with *ortho* H_b protons (*ortho* coupling).

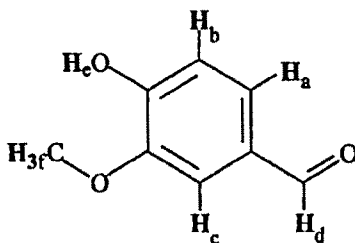
H_b and H_c protons appear as (2H, d) (two proton, doublet) each. H_b and H_c protons actually form a complex AA' BB' system of *p*-disubstituted benzene derivative where the substituents are different. As a result they represent a pair of doublets where H_b protons couple with H_c protons and *vice versa*.

- (c) $\delta = 4.30$ is assigned to two H_a protons of $\text{Ar}-\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{CH}_2\text{Br} \end{array}$. H_a protons appear as (2H, s) (two proton, singlet) as there is no adjacent hydrogen to couple with. H_a protons are deshielded due to (-I) effect of $\text{C}=\text{O}$ group and Br.

- (d) $\delta = 2.34$ is assigned to three H_d protons of $\text{dH}_3\text{C}-\text{C}_6\text{H}_4-\text{C}(=\text{O})\text{CH}_2\text{Br}$. These benzylic protons (H_d) appear as (3H, s) (three proton, singlet) as there is no adjacent hydrogen to couple with.

3. ^1H NMR Spectrum of Vanillin

The spectrum was recorded in 300 MHz instrument in CDCl_3 solvent using TMS as internal standard.



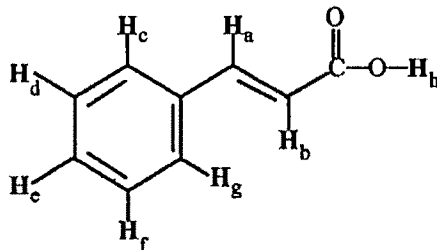
	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	9.8	s	1	H_d proton (aldehyde $\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{H}_d \end{array}$ proton)
(b)	7.35-7.45	m	2	H_a and H_c protons (aromatic)
(c)	7.05	d	1	H_b proton (aromatic)
(d)	6.7	br, s	1	H_e proton of phenolic $-\text{OH}_e$ group
(e)	3.85	s	3	H_f protons of $\text{Ar}-\text{OCH}_3$

CHP 34a

- (a) $\delta = 9.8$ is assigned to H_d proton of $\begin{array}{c} O \\ || \\ -C-H_d \end{array}$. H_d proton is highly deshielded due to diamagnetic anisotropic effect and $(-I)$ effect of $C=O$ group. H_d proton appears as (1H, s) (one proton, singlet).
- (b) $\delta = 7.45, 7.35$ are assigned to two aromatic protons H_a and H_c respectively which are *ortho* to $-CHO$ group. H_a and H_c are deshielded by the $(-I)$ and diamagnetic anisotropy of aldehyde $C=O$ group but are less deshielded compared to aldehydic H_d proton ($\begin{array}{c} O \\ || \\ -C-H_d \end{array}$) due to larger distance from $C=O$ group. H_a and H_c appear as (2H, m) (two proton, multiplet), since H_c couples with H_e (*meta*).
- (c) $\delta = 7.05$ is assigned to H_b proton (H_b is *meta* to $-CHO$ group and *ortho* to phenolic $-OH$ group) which is shielded by $(+R)$ effect of $-\ddot{O}H$ Group. H_b proton appears as a (1H, d) (one proton, doublet) as it couples with *ortho* proton H_a . (*ortho* coupling)
- (d) $\delta = 6.7$ is assigned to H_e proton of $Ar'-OH_e$ which appears as a broad singlet (br. s) due to intermolecular hydrogen bonding. H_e is deshielded due to anisotropy of the benzene ring and resonance that takes away electron density from the oxygen of the phenolic $-OH$ group. But the deshielding is less prominent because of electron rich environment of *ortho* $-\ddot{O}CH_3$ group with lone pairs of electrons present on oxygen atom.
- (e) $\delta = 3.85$ is assigned to H_f protons of $Ar-\ddot{O}CH_{3f}$. H_f protons are less deshielded due to larger distance from the anisotropy of the benzene ring. H_f proton appear as (3H, s) (three proton, singlet) as they have no neighbouring hydrogen to couple with. OCH_{3f} protons are deshielded than normal methyl protons since they are attached to electronegative oxygen atom.

4. 1H NMR Spectrum *trans*-Cinnamic Acid

The spectrum was recorded in 300 MHz instrument in $CDCl_3$ solvent using TMS as internal standard.



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	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	12.7	br. s	1	H_h proton of $\text{Ph} = \text{CH} - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{O} - \text{H}_h'$
(b)	7.8	d	1	H_a proton of $\text{PhCH}_a = \text{CHCOOH}$
(c)	7.56	m	2	H_c and H_g protons <i>ortho</i> to $-\text{CH}=\text{CHCOOH}$ group (aromatic)
(d)	7.42	m	3	H_d , H_e and H_f protons (aromatic)
(e)	6.45	d	1	H_b proton of $\text{PhCH}=\text{CH}_b\text{COOH}$

(a) $\delta = 12.7$ is assigned to H_h proton of $\text{PhCH} = \text{CH} - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{O} - \text{H}_h$. **Intermolecular**

hydrogen bonding decreases electron density around H_h atom of $-\overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{OH}_h$ group. As a result, H_h proton is most deshielded and comes as a broad singlet (br. s).

(b) $\delta = 7.8$ is assigned to H_a proton of $\text{PhCH}_a = \text{CHCOOH}$. This vinylic proton is deshielded due to diamagnetic anisotropy of the benzene ring. H_a appears as a (1H, d) (one proton, doublet) as it couples with adjacent H_b proton and also due to positive charge created on H_a bearing carbon atom due to conjugation with $-\text{COOH}$ group.

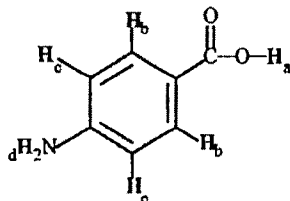
(c) $\delta = 7.56$ is assigned to two aromatic protons H_c and H_g which are present *ortho* to $-\text{CH}=\text{CH}-\text{COOH}$ group. These two protons are deshielded due to diamagnetic anisotropic effect of the benzene ring and C=C double bond and appears as a (2H, m) (two proton, multiplet) signal.

(d) $\delta = 7.42$ is assigned to three aromatic protons H_d , H_e and H_f . These three protons are less deshielded compared to H_c and H_g protons as they do not fall in the deshielding region of C=C bond. H_d , H_e and H_f give rise to a (3H, m) (three proton, multiplet) signal.

(e) $\delta = 6.45$ is assigned to H_b proton of $\text{Ph}-\text{CH}=\text{CH}_b\text{COOH}$. Due to larger distance from the benzene ring, H_b is less deshielded compared to H_a and (-R) effect of $-\text{COOH}$ group does not have any effect on carbon atom bearing H_b . H_b appears as a (1H, d) (one proton, doublet) as it couples with neighbouring H_a proton. Thus H_a and H_b appear as a pair of doublets.

5. ^1H NMR Spectrum of *p*-Aminobenzoic Acid (4-Aminobenzoic acid)

The spectrum was recorded in 300 MHz instrument in CDCl_3 and $\text{DMSO}-d_6$ solvent using TMS as internal standard.



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	12.00	br. s	1	H_a proton of $\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}_a$
(b)	7.7	d	2	Two H_b protons <i>ortho</i> to $-\text{COOH}$ group (aromatic)
(c)	6.6	d	2	Two H_c protons <i>ortho</i> to $-\text{NH}_2$ and <i>meta</i> to $-\text{COOH}$ groups (aromatic)
(d)	5.9	br. s	2	H_d protons of $\text{Ar}-\text{NH}_{2d}$.

- (a) $\delta = 12.00$ is assigned to H_a proton of $\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}_a$. Intermolecular hydrogen bonding decreases electron density around the hydrogen atom of $-\text{C}-\text{O}-\text{H}_a$ group and so H_a becomes most deshielded. H_a appears as a (one proton, broad singlet) (1H, br. s).
- (b) $\delta = 7.7$ is assigned to two aromatic H_b protons which are present *ortho* to $-\text{COOH}$ group. These two protons are deshielded due to $(-R)$ and diamagnetic anisotropy of $\text{C}=\text{O}$ of $-\text{COOH}$ group. These two electron withdrawing effects decrease the electron density around the H_b protons. They appear as two proton, doublet (2H, d) due to coupling with two *ortho* protons (H_c), (*ortho* coupling).
- (c) $\delta = 6.6$ is assigned to two aromatic H_c protons which are *ortho* to $-\text{NH}_2$ group and *meta* to $-\text{COOH}$ group. H_c protons are shielded by the $(+R)$ effect of $-\ddot{\text{N}}\text{H}_2$ group which increases the electron density around these protons. H_c protons appear as a two proton, doublet (2H, d) due to coupling with two *ortho* protons (H_b) (*ortho* coupling).

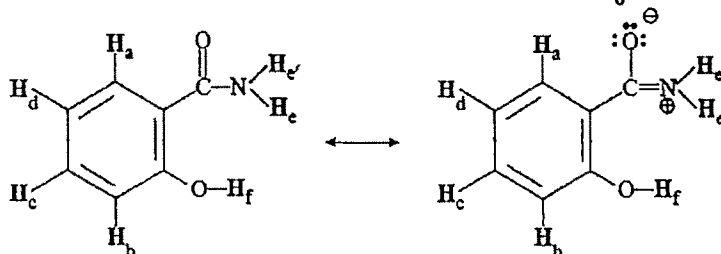
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In fact, H_b and H_c protons constitute complex AA' BB' type spectrum of *p*-disubstituted benzene derivative with different substituents and appear as a pair of doublet each.

- (d) $\delta = 5.9$ is assigned to two H_d protons of ${}_dH_2N-Ar$. **Intermolecular hydrogen bonding** is there and H_d protons appear as a two proton, broad singlet (2H, br. s) signal. The broad singlet is due to **intermolecular hydrogen bonding**.

6. 1H NMR Spectrum of Salicylamide

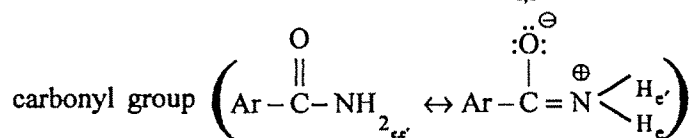
The spectrum was recorded in 300 MHz instrument in $DMSO-d_6$. Solvent using TMS as internal standard



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	13.4	br. s	1	H_f proton of $Ar-OH_f$
(b)	8.42	two br. s	2	H_e and $H_{e'}$ protons of $Ar-\overset{\overset{O}{\parallel}}{C}-N\begin{matrix} H_{e'} \\ H_e \end{matrix}$
(c)	7.8	d	1	H_a proton (aromatic)
(d)	7.4	t	1	H_c proton (aromatic)
(e)	6.75-6.8	m	2	H_d and H_b protons (aromatic)

- (a) $\delta = 13.4$ is assigned to H_f proton of $Ar-OH_f$. **Intramolecular hydrogen bonding** decreases the electron density around the H atom of $Ar-OH_f$ and makes it most deshielded. H_f appears as a one proton, broad singlet (1H, br. s).

- (b) $\delta = 8.42$ is assigned to H_e of $-\overset{\overset{O}{\parallel}}{C}-NH_{2_{e,e'}}$ where H_e lies *trans* to 'O' atom of amide



$\delta = 7.85$ is assigned to $H_{e'}$ of $-\overset{\overset{O}{\parallel}}{C}-NH_{2e'}$, where $H_{e'}$ lies *cis* to O atom of amide carbonyl group.

As a result, the two amide protons (H_e , $H_{e'}$) are in magnetically different environment and resonate at different chemical shift values. Each of H_e and $H_{e'}$ appears as a broad singlet (br. s).

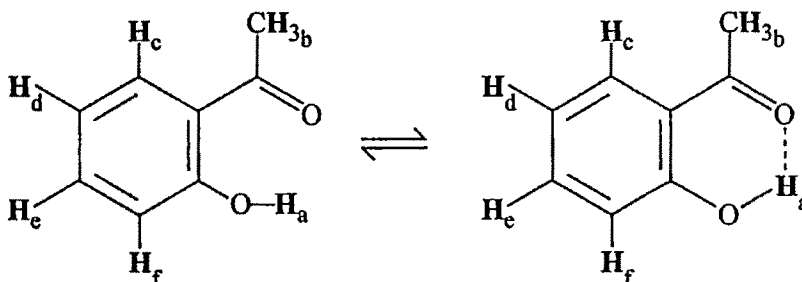
- (c) $\delta = 7.8$ is assigned to aromatic H_a proton which is *ortho* to $-\overset{\overset{O}{\parallel}}{C}-NH_2$ and *meta* to phenolic $-OH$ group. H_a is deshielded due to ($-R$), ($-I$) and diamagnetic anisotropy of amide carbonyl group. H_a comes as a one proton, doublet (1H, d) as it couples with *ortho* H_d proton. (*ortho* coupling).

- (d) $\delta = 7.4$ is assigned to aromatic H_c proton which is *para* to $-\overset{\overset{O}{\parallel}}{C}-NH_2$ group and *meta* to phenolic $-OH$ group. H_c proton is deshielded by the ($-R$) effect of carbonyl of $-\overset{\overset{O}{\parallel}}{C}-NH_2$ group. H_c proton appears as a one proton triplet (1H, t) as it couples with two *ortho* protons H_b and H_d (*ortho* coupling).

- (e) $\delta = 6.75 - 6.8$ is assigned to two aromatic protons H_b and H_d which are *meta* to $-\overset{\overset{O}{\parallel}}{C}-NH_2$ group and get shielded by ($+R$) effect of $-\ddot{O}H$ Group. H_b and H_d appear as a two proton, multiplet (2H, m), since H_b couples with H_c and H_d couples with H_a and H_c .

7. 1H NMR Spectrum of *o*-Hydroxyacetophenone (2-Hydroxyacetophenone)

The spectrum was recorded in 300 MHz instrument in $CDCl_3$ and $DMSO-d_6$ solvent using TMS as internal standard.



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	12.3	br. s	1	H_a proton of $Ar-OH_a$
(b)	7.84	dd	1	H_c proton (aromatic)
(c)	7.5	t	1	H_e proton (aromatic)
(d)	6.9-7.0	m	2	H_d and H_f protons (aromatic)
(e)	2.63	s	3	H_b protons of $Ar-\overset{\overset{O}{ }}{C}-CH_{3b}$

- (a) $\delta = 12.3$ is assigned to H_a proton of $Ar-OH_a$. Intramolecular hydrogen bonding decreases the electron density around the hydrogen atom of $Ar-OH_a$ making it most deshielded and H_a appears as a one proton, broad singlet (1H, br. s). The broad nature of singlet is due to intramolecular hydrogen bonding.

- (b) $\delta = 7.84$ is assigned to aromatic H_c proton which is *ortho* to $-\overset{\overset{O}{||}}{C}-CH_3$ group and *meta* to phenolic $-OH$ group. H_c is deshielded due to $(-R)$ effect and diamagnetic anisotropic effect of $C=O$ group. It appears as a one proton, double doublet (1H, dd) as it couples with *ortho* proton H_d (*ortho* coupling) and *meta* proton H_e (*meta* coupling).

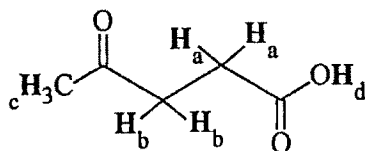
- (c) $\delta = 7.5$ is assigned to aromatic H_e proton which is *para* to $-\overset{\overset{O}{||}}{C}-CH_3$ group and *meta* to phenolic $-OH$ group. H_e is deshielded by the $(-R)$ effect of $C=O$ group but is less deshielded compared to H_c proton as the former does not fall in the deshielding zone of $C=O$ group. H_e appears as a one proton triplet (1H, t) as it couples with two *ortho* protons namely H_d and H_f (*ortho* coupling).

- (d) $\delta = 6.9-7.0$ is assigned to two aromatic protons H_d and H_f which are *meta* to $-\overset{\overset{O}{||}}{C}-CH_3$ group and *para* and *ortho* to phenolic $-OH$ group respectively. The $(+R)$ effect of $-OH$ Group increases the electron density around H_d and H_f and shield them. The signal comes as a two proton, multiplet (2H, m).

- (e) $\delta = 6.9-7.0$ is assigned to H_b protons of $Ar-\overset{\overset{O}{||}}{C}-CH_{3b}$. These keto methyl (H_b protons) protons are a bit deshielded by the $(-I)$ and $(-R)$ effects of $C=O$ group which decrease the electron density around them. H_b protons appear as a three proton, singlet (3H, s) signal due to absence of any adjacent hydrogen atom to couple with.

8. ^1H NMR Spectrum of 4-Ketopentanoic acid (4-Oxopentanoic Acid) (Laevulinic Acid)

The spectrum was recorded in 300 MHz instrument in CDCl_3 solvent using TMS as internal standard.



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	10.8	br. s	1	H_d proton of $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}_d$
(b)	2.7	t	2	H_b protons of $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_{2b}-\text{CH}_2\text{COOH}$
(c)	2.57	t	2	H_a protons of $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_{2a}-\text{COOH}$
(d)	2.2	s	3	H_c protons of $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\text{COOH}$

(a) $\delta = 10.8$ is assigned to H_d proton of $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}_d$. **Intermolecular hydrogen bonding** decreases the electron density around H_d atom of $-\text{COOH}_d$ group and the proton becomes most deshielded. Due to this intermolecular hydrogen bonding, H_d appears as a one proton, broad singlet (1H, br. s).

(b) $\delta = 2.7$ is assigned to two H_b protons of $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_{2b}-\text{CH}_2\text{COOH}$. These two protons are deshielded due to $(-I)$ effect of $\text{C}=\text{O}$ group and they fall in the deshielding zone of $\text{C}=\text{O}$ group of keto methyl moiety. H_b protons appear as two proton, triplet (2H, t) signal as they couple with two adjacent H_a protons.

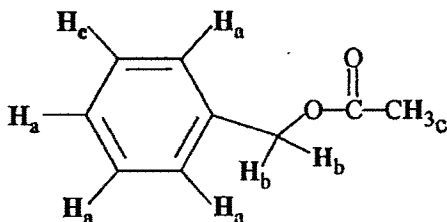
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(c) $\delta = 2.57$ is assigned to two H_a protons of $H_3C-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_{2a}-\overset{\overset{O}{\parallel}}{C}-OH$. H_a protons are deshielded by (-I) effect of $C=O$ group of $-COOH$. But they appear to be less deshielded compared to H_b protons as the (-I) effect of $-\overset{\overset{O}{\parallel}}{C}-CH_3$ group is more than the (-I) effect of $-COOH$ group. H_a protons appear as two proton, triplet (2H, t) as they couple with two adjacent H_b protons.

(d) $\delta = 2.2$ is assigned to H_c protons of $H_{3c}C-\overset{\overset{O}{\parallel}}{C}-CH_2CH_2COOH$. These three protons are a bit deshielded due to (-I) effect of $C=O$ group. H_c protons appear as three-proton, singlet (3H, s) due to absence of any adjacent hydrogen atom to couple with.

9. 1H NMR Spectrum of Benzyl Acetate

The spectrum was recorded in 300 MHz instrument in $CDCl_3$ solvent using TMS as internal standard.



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	7.35	s	5	H_a protons (all aromatic)
(b)	5.1	s	2	H_b protons (benzylic) of $Ph-CH_{2b}-O-COCH_3$
(c)	2.1	s	3	H_c protons of $ \begin{array}{c} O \\ \parallel \\ PhCH_2O-C-CH_{3c} \end{array} $

CHP 34a

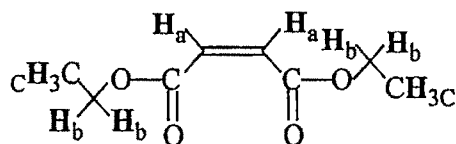
(a) $\delta = 7.35$ is assigned to five aromatic H_a protons. Benzyl acetate represents a typical example which manifests **deceptive simplicity**. So all the five aromatic protons (H_a) resonate at the same chemical shift values, and appears as a five proton singlet peak (5H, s).

(b) $\delta = 5.1$ is assigned to two benzylic H_b protons of $\text{Ph}-\text{CH}_{2b}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$. H_b protons are deshielded by the anisotropy of the benzene ring and also by the electronegativity of adjacent oxygen atom. H_b protons appear as two proton, singlet (2H, s) as there is no adjacent hydrogen atom to couple with.

(c) $\delta = 2.1$ is assigned to three H_c protons of $\text{Ph}-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_{3c}$. These three H_c protons are comparatively less deshielded with respect to benzylic (H_b) protons. H_c protons appear as three proton, singlet (3H, s) as there is no adjacent hydrogen atom to couple with.

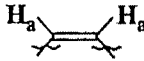
10. ^1H NMR Spectrum of Diethyl Maleate

The spectrum was recorded in 300 MHz instrument in CDCl_3 solvent using TMS as internal standard.



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	6.2	s	2H (1)	H_a (vinyl) protons of
(b)	4.2	q	4H (2)	H_b protons of $\begin{array}{c} \text{O} \\ \parallel \\ (= \text{CH} - \text{C} - \text{OCH}_{2b}\text{CH}_3)_2 \end{array}$
(c)	1.24	t	6H (3)	H_c protons of $\begin{array}{c} (-\text{CH} - \text{C} - \text{OCH}_2\text{CH}_{3c})_2 \\ \parallel \\ \text{O} \end{array}$

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- (a) $\delta = 6.2$ is assigned to two vinylic H_a protons of  moiety where they lie *cis* to each other. H_a protons are most deshielded by the diamagnetic anisotropy of C=C double bond and appear as two proton, singlet (2H, s).

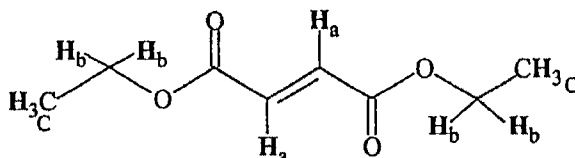
- (b) $\delta = 4.2$ is assigned to four H_b protons of $(=CH-\overset{\overset{O}{\parallel}}{C}-OCH_2CH_3)_2$. These four protons (α -hydrogens of an ester) are deshielded due to electronegativity of adjacent oxygen atom. H_b protons appear as four proton, quartet (4H, q) as they couple with three adjacent H_c protons.

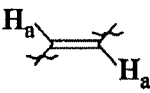
- (c) $\delta = 1.24$ is assigned to six H_c protons of $(-CH-\overset{\overset{O}{\parallel}}{C}-OCH_2CH_3)_2$. H_c protons are

maximum shielded due to larger distance from the anisotropic effect of C=C double bond and also not present adjacent to any electronegative oxygen atom. H_c protons give rise to six proton, triplet (6H, t) signal as they couple with two adjacent H_b protons.

11. 1H NMR Spectrum of Diethyl Fumarate

The spectrum was recorded in 300 MHz instrument in $CDCl_3$ solvent using TMS as internal standard.



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	6.8	s	2H(1)	H_a (vinylic) protons of  moiety
(b)	4.19	q	4H(2)	H_b protons of $\begin{array}{c} O \\ \parallel \\ (=CH-C-OCH_2CH_3)_2 \end{array}$
(c)	1.30	t	6H(3)	H_c protons of $\begin{array}{c} O \\ \parallel \\ (=CH-C-OCH_2-CH_3)_2 \end{array}$

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- (a) $\delta = 6.8$ is assigned to two vinylic H_a protons which lie *trans* to each other. H_a protons are most deshielded by the diamagnetic anisotropy of $C=C$ double bond and appear as two proton, singlet ($2H$, s).

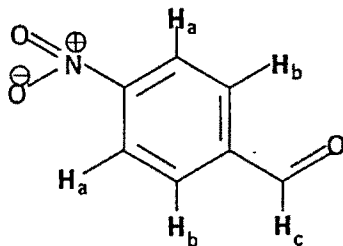
- (b) $\delta = 4.19$ is assigned to four H_b protons ($=CH-\overset{\overset{O}{\parallel}}{C}-OCH_2CH_3$)₂. These four protons (α -hydrogens of an ester) are deshielded by the electronegativity of adjacent oxygen atom. H_b protons appear as four proton, quartet ($4H$, q) as they couple with three adjacent H_c protons.

- (c) $\delta = 1.24$ is assigned to six H_c protons of ($-CH-\overset{\overset{O}{\parallel}}{C}-OCH_2CH_3$)₂. H_c protons are

maximum shielded due to larger distance from the anisotropic effect of $C=C$ double bond and also not present adjacent to any electronegative oxygen atom. H_c protons give rise to six proton, triplet ($6H$, t) signal as they couple with adjacent two H_b protons.

12. ¹H NMR Spectrum of *p*-Nitrobenzaldehyde (4-Nitrobenzaldehyde)

The spectrum was recorded in 300 MHz instrument in CDCl₃ solvent using TMS as internal standard.



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	10.2	s	1	Aldehydic H_c proton of $\begin{array}{c} O \\ \parallel \\ Ar-C-H_c \end{array}$
(b)	8.42	d	2	H_a protons (aromatic)
(c)	8.14	d	2	H_b protons (aromatic)

- (a) $\delta = 10.2$ is assigned to aldehydic H_c proton of $Ar-\overset{\overset{O}{\parallel}}{C}-H_c$. H_c is most deshielded due to diamagnetic anisotropy of $C=O$ group and also by the ($-I$) and ($-R$) effects of $C=O$

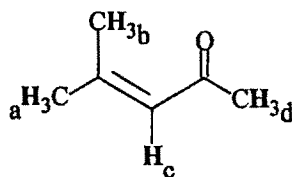
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group. These effects decrease the electron density around the H_c proton of $-\overset{\overset{O}{||}}{C}-H_c$ and make it resonate at a higher chemical shift value.

- (b) $\delta = 8.42$ is assigned to two aromatic H_a protons which are present *ortho* to $-\text{NO}_2$ group and *meta* to $-\text{CHO}$ group. ($-\text{R}$) effect of $-\text{NO}_2$ group decreases the electron density around the two H_a atoms and make them deshielded. H_a protons are also deshielded by the diamagnetic anisotropy of $\text{N}=\text{O}$ bond of $-\text{NO}_2$ group. H_a protons appear as two proton, doublet (2H, d) as they couple with *ortho* H_b protons (*ortho* coupling).
- (c) $\delta = 8.14$ is assigned to two aromatic H_b protons which are present *ortho* to $-\text{CHO}$ group and *meta* to $-\text{NO}_2$ group. Two H_b protons are deshielded by ($-\text{R}$) and ($-\text{I}$) effects of $-\text{CHO}$ group and also by the diamagnetic anisotropy of $\text{C}=\text{O}$ bond of $-\text{CHO}$. But H_b protons are less deshielded than H_a protons because ($-\text{I}$) effect of $-\text{NO}_2$ group is stronger than that of $-\text{CHO}$ group. H_b protons appear as two proton, doublet (2H, d) as they couple with *ortho* H_a proton. (*ortho* coupling). In practice, both H_a and H_b protons give rise to a pair of doublets as they actually represent complex AA' BB' system of p-disubstituted benzene derivative with different substituents.

13. ^1H NMR Spectrum of Mesityl Oxide

The spectrum was recorded in 300 MHz instrument in CDCl_3 solvent using TMS as internal standard.



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	6.08	s	1	H_c (vinyllic) proton of $\begin{array}{c} \text{Me}_2\text{C} = \text{C} - \text{COCH}_3 \\ \\ H_c \end{array}$
(b)	2.16	s	3	H_d (keto methyl protons) of $\begin{array}{c} \text{O} \\ \\ \text{Me}_2\text{C} = \text{CH} - \text{C} - \text{CH}_{3d} \end{array}$

	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(c)	2.12	s	3	H_b protons of $H_3C - \overset{\overset{CH_{3b}}{ }}{C} = CH - \overset{\overset{O}{ }}{C} - CH_3$ ($-CH_{3b}$ is <i>cis</i> to $-\overset{\overset{O}{ }}{C}-CH_3$ group)
(d)	1.91	s	3	H_a protons of $H_3C - \overset{\overset{CH_{3a}}{ }}{C} = CH - \overset{\overset{O}{ }}{C} - CH_3$

- (a) $\delta = 6.08$ is assigned to vinylic H_c proton of $Me_2C = \underset{\underset{H_c}{|}}{C} - COCH_3$. H_c proton is

deshielded by the (-I) effect of C=O group. The signal appears as one proton, singlet (1H, s) for H_c proton which is the most deshielded one.

[NOTE : H_c may appear as (1H, m) due to long range 4-bond allylic coupling where H_c couples with hydrogens of both the methyl groups of $Me_2C=$ moiety.]

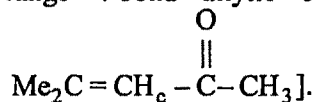
- (b) $\delta = 2.16$ is assigned to three H_d protons of $Me_2C = CH - \overset{\overset{O}{||}}{C} - CH_{3d}$. These protons are deshielded by the (-I) effect of C=O group which decreases electron density around them. H_d protons appear as three proton, singlet (3H, s) as there is no adjacent hydrogen atom to couple with.

- (c) $\delta = 2.12$ is assigned to three H_b protons of $H_3C - \overset{\overset{CH_{3b}}{|}}{C} = CH - \overset{\overset{O}{||}}{C} - CH_3$. H_b protons are deshielded by the diamagnetic anisotropy of C=C double bond and they also fall to some extent in the deshielding zone of C=O group. They appear as three proton, singlet (3H, s) in the spectrum.

[NOTE : H_b protons may appear as three proton, multiplet (3H, m) due to long

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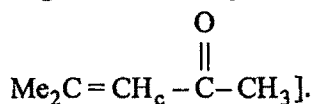
range 4-bond allylic coupling where H_b protons couple with H_c proton of



- (d) $\delta = 1.91$ is assigned to three H_a protons of $\text{H}_3\text{C}-\underset{\text{CH}_{3a}}{\underset{|}{\text{C}}}=\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$. H_a protons

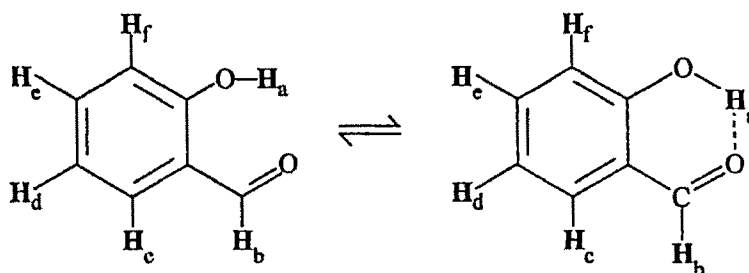
are deshielded by the diamagnetic anisotropy of $\text{C}=\text{C}$ double bond but are less deshielded as they do not fall in the deshielding zone of $\text{C}=\text{O}$ group. H_a protons appear as three-proton, singlet (3H, s) in the spectrum.

[NOTE : H_a protons also may appear as three proton, singlet (3H, m) due to long range 4-bond allylic coupling where H_a protons couple with H_c proton of



14. ^1H NMR Spectrum of Salicylaldehyde (2-Hydroxybenzaldehyde)

The spectrum was recorded in 300 MHz instrument in CDCl_3 solvent using TMS as internal standard.



	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	10.75	s	1	H_a proton of $\text{Ar}-\text{OH}_a$.
(b)	10.1	s	1	H_b proton (aldehyde proton) of $\text{Ar}'-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}_b$

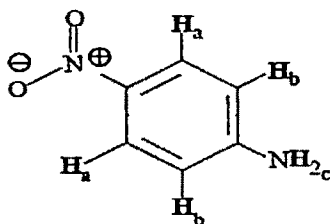
	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(c)	7.5-7.6	m	2	H_c and H_e protons (aromatic)
(d)	6.95	m	2	H_d and H_f protons (aromatic)

- (a) $\delta = 11.05$ is assigned to H_a proton of $Ar-O-H_a$. **Intramolecular hydrogen bonding** decreases electron density around H_a atom of $Ar-OH_a$ making it most deshielded. H_a proton comes as one proton, singlet (1H, s) in the spectrum as a sharp peak as salicylaldehyde forms an intramolecular hydrogen bond.
- (b) $\delta = 9.8$ is assigned to H_b proton (aldehyde proton) of $Ar'-C(=O)-H_b$. H_b proton is

$$\begin{array}{c} \text{O} \\ || \\ Ar'-C-H_b \end{array}$$
deshielded due to diamagnetic anisotropic effect of $C=O$ group as well as by the $(-I)$ effect of $C=O$ group which decreases the electron density around aldehydic H_b proton. H_b proton appears as one proton, singlet (1H, s) in the spectrum.
- (c) $\delta = 7.5-7.6$ is assigned to aromatic H_c proton which is *ortho* to $-CHO$ group and to H_e proton (aromatic) *para* to $-CHO$ group. The protons are deshielded by the diamagnetic anisotropy and $(-R)$ effect of $C=O$ group which decreases the electron density around them. H_c and H_e protons appear as two proton, multiplet (2H, m).
- (d) $\delta = 6.95$ is assigned to two aromatic H_d and H_f protons which are respectively *para* and *ortho* to $-OH$ group. $(+R)$ effect of $-O^-$ group increases the electron density around H_d and H_f hydrogen atoms making them shielded. H_d and H_f protons appear as two proton, multiplet (2H, m) in the spectrum.

15. 1H NMR Spectrum of *p*-Nitroaniline (4-Nitroaniline)

The spectrum was recorded in 300 MHz instrument in $CDCl_3$ and $DMSO-d_6$ solvent using TMS as internal standard.



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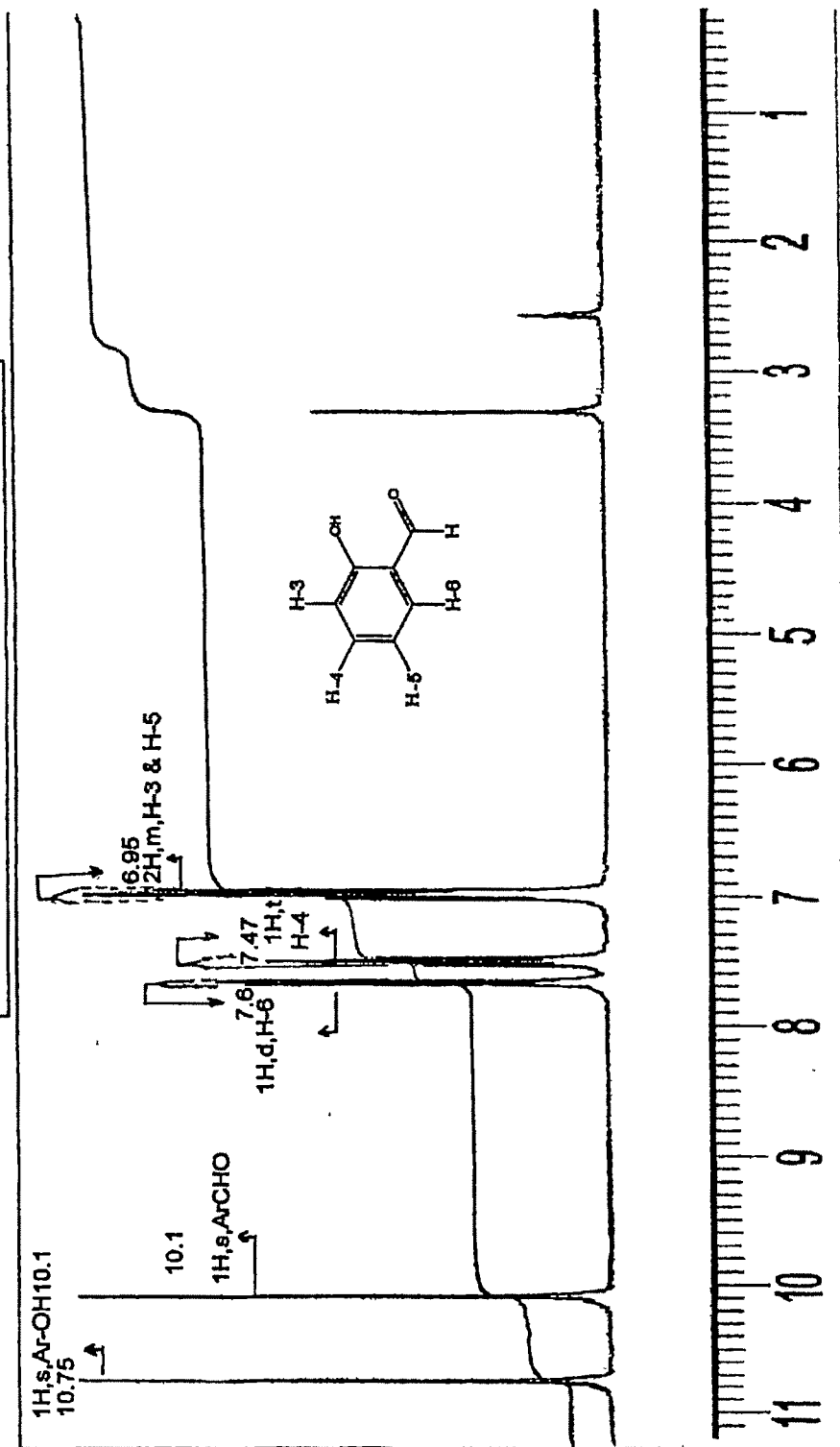
	Chemical shift (in δ ppm)	Splitting Pattern	Relative ratio of H's	Probable Assignment
(a)	7.94	d	2	Two H_a protons (aromatic)
(b)	6.63	d	2	Two H_b protons (aromatic)
(c)	6.4	br. s	2	H_c protons of $Ar-NH_{2c}$

- (a) $\delta = 7.94$ is assigned to two aromatic H_a protons *ortho* to $-NO_2$ group. ($-R$) effect of $-NO_2$ group decreases the electron density around H_a protons and they also fall in the deshielding zone of $N=O$ bond of $-NO_2$ group. As a result H_a protons are deshielded and appear as two protons, doublet (2H, d) due to coupling with two *ortho* H_b protons (*ortho* coupling).
- (b) $\delta = 6.63$ is assigned to two aromatic H_b protons *ortho* to $-NH_2$ group. ($+R$) effect of $-NH_2$ group increases the electron density around H_b protons and make them comparatively shielded. H_b protons appear as two proton, doublet (2H, d) due to coupling with two *ortho* H_a protons (*ortho* coupling).
 H_a and H_b form a pair of two proton doublet (2H, d) each as they constitute a complex $AA' BB'$ system of *p*-disubstituted benzene derivative with different substituents.
- (c) $\delta = 6.4$ is assigned to two H_c protons of $Ar-NH_{2c}$. These two protons are deshielded due to anisotropy of the benzene ring and resonance that takes away electron density around H_c protons of $Ar-NH_{2c}$ which leads to change of hybridisation of N atom. H_c protons appear as two protons, singlet (2H, s) in the spectrum because there is no adjacent hydrogen atom to couple with.

Assignment of ^1H NMR spectrum of 2-hydroxybenzaldehyde

^1H NMR SPECTRUM OF 2-HYDROXYBENZALDEHYDE

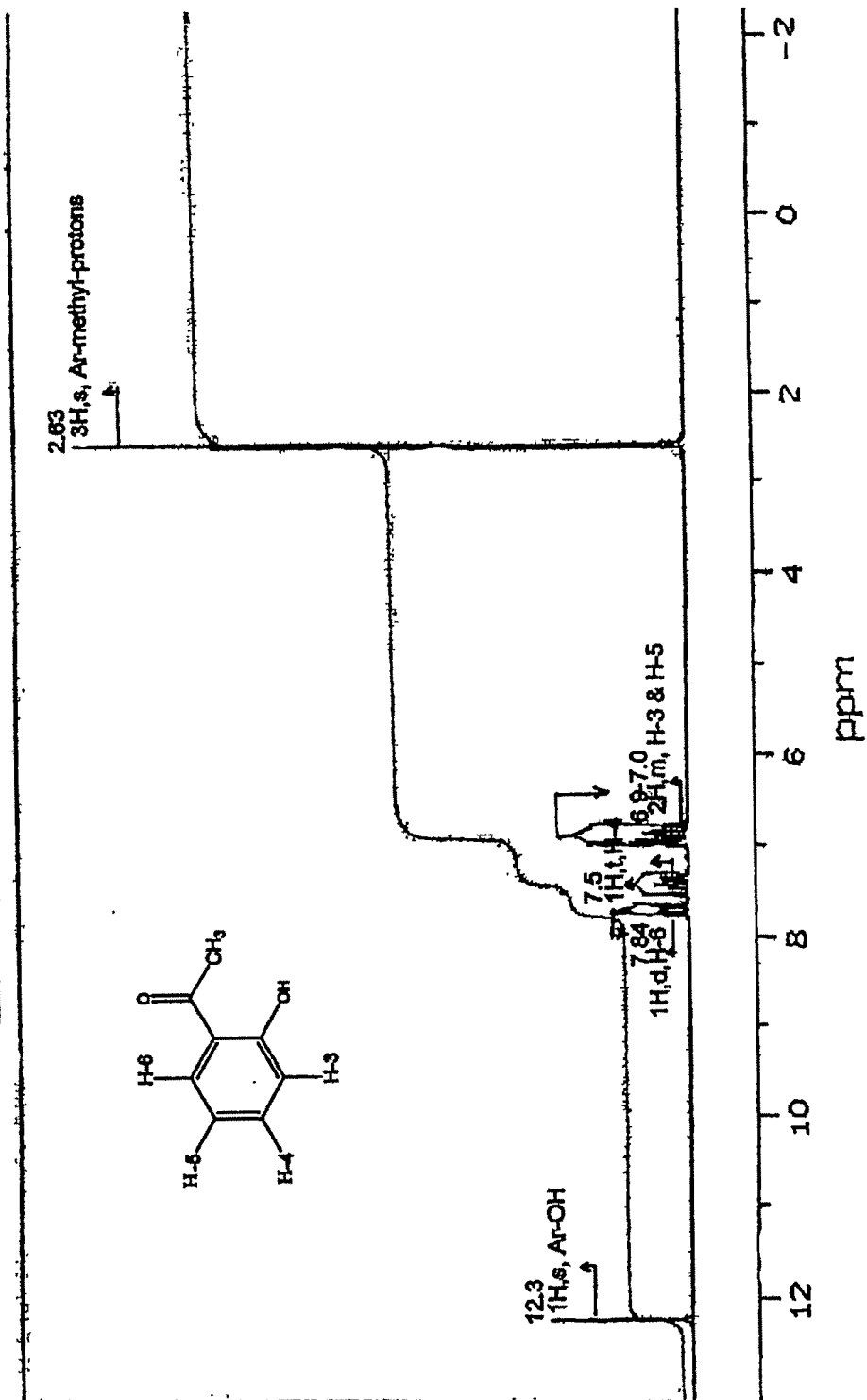
δ VALUE: 10.75, 10.1, 7.6, 7.47, 6.95

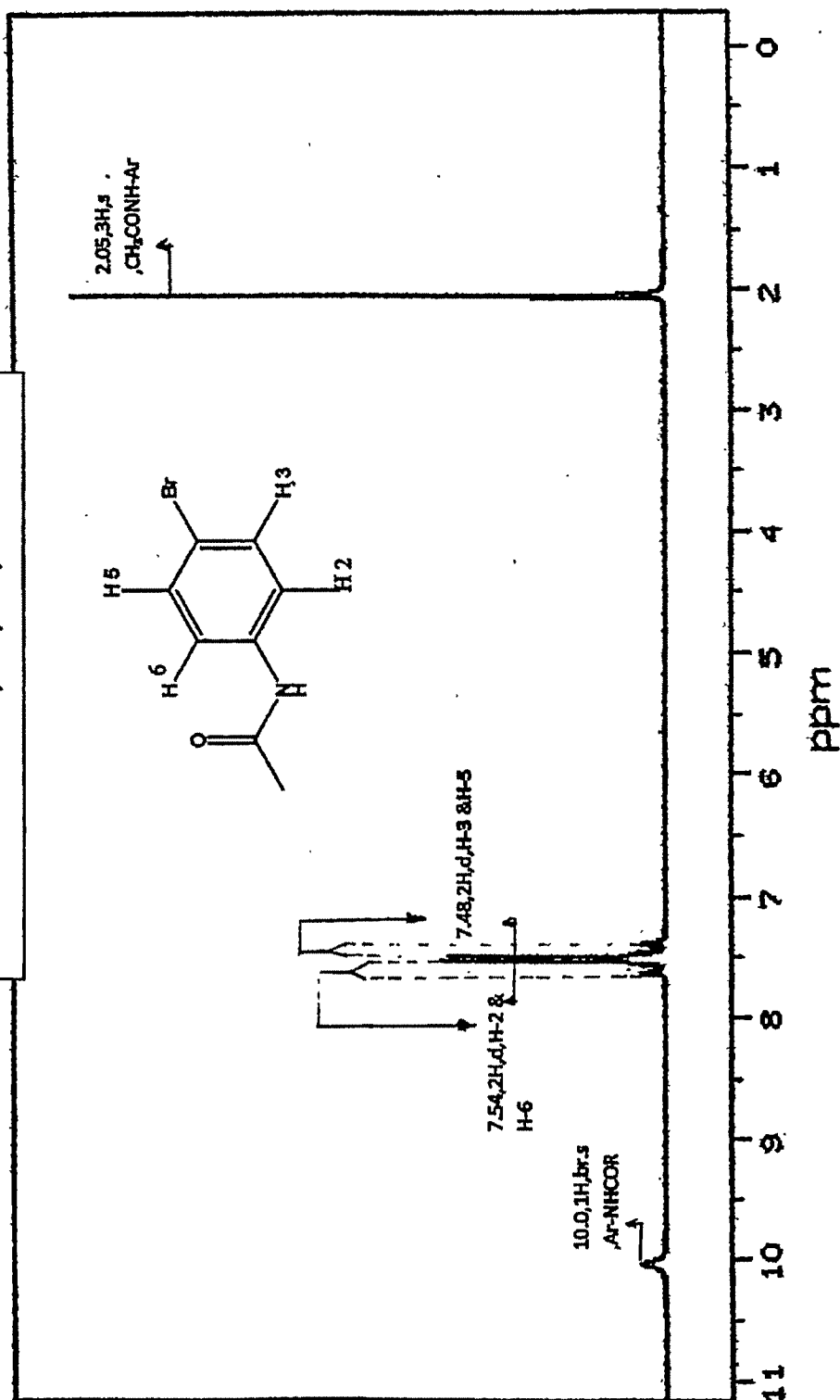


Assignment of ^1H NMR spectrum of 2-hydroxyacetophenone

^1H NMR SPECTRUM OF 2-HYDROXYACETOPHENONE

δ VALUE: 12.3, 7.84, 7.5, 6.9-7.0, 2.63

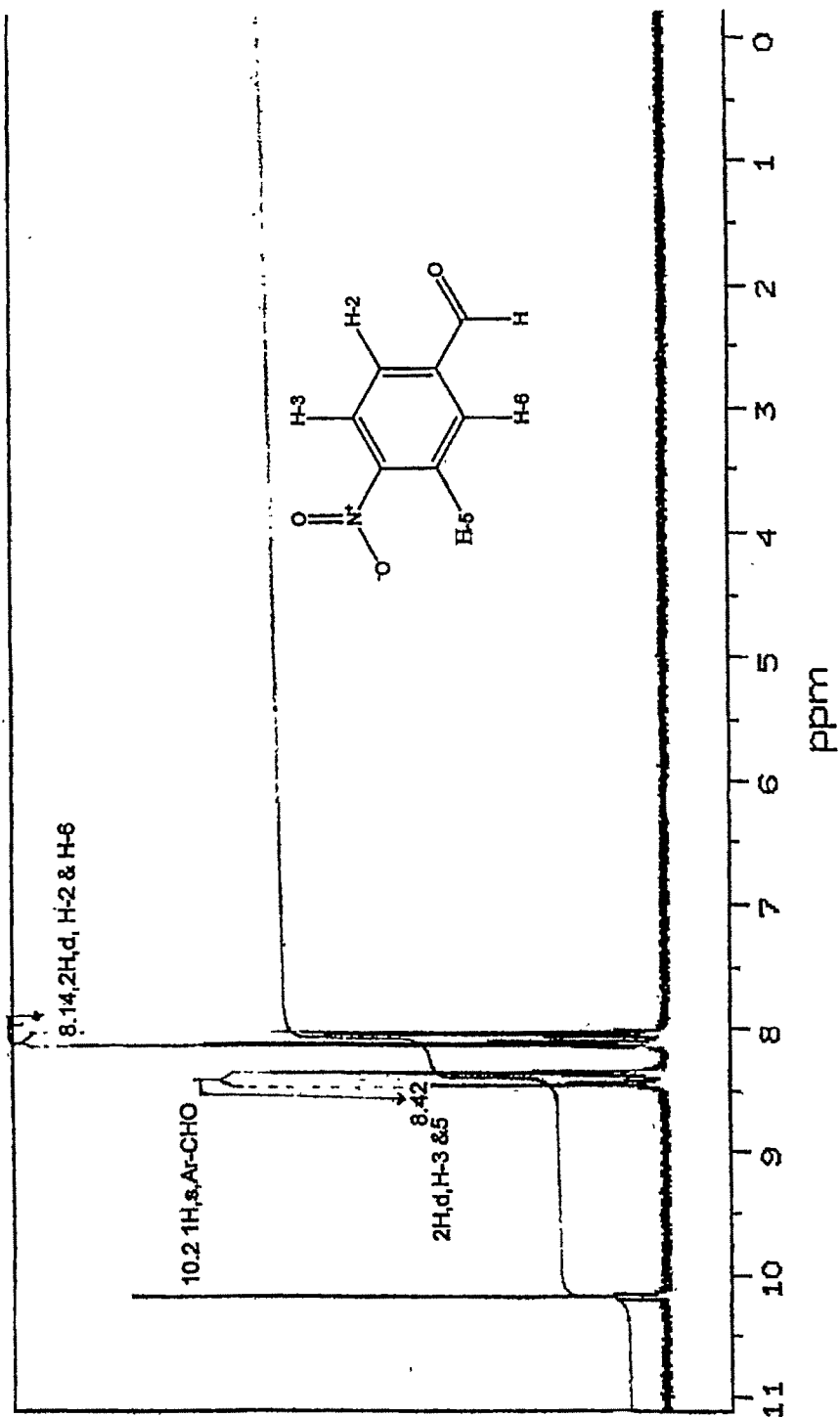


Assignment of ^1H NMR spectrum 4-bromoacetanilide **^1H NMR SPECTRUM OF 4-BROMOACETANILIDE** **δ VALUE: 10.0, 7.54, 7.48, 2.05**

Assignment of ^1H NMR spectrum of 4-nitrobenzaldehyde

^1H NMR SPECTRUM OF 4-NITROBENZALDEHYDE

δ VALUE: 8.14, 8.42, 10.2



CHP 34b

Qualitative Analysis of a Single Solid Organic Compound

Sample Number :

Physical Characteristics:

(i) Colour:

(ii) Texture:

(iii) Odour:

Detection of Special Elements (N, Cl, S) by Lassaigne's Method :

Lassaigne's Test : A pea sized dry and clean sodium was taken in a fusion tube and heated gently until it melted with a shiny surface. A pinch of the sample was added to it and the mixture was heated gently and then strongly to red hot on a non-luminous flame for about two minutes. Finally the fusion tube was carefully plunged in a mortar containing *distilled water* (8-10 mL). The mixture was ground thoroughly by a pestle and filtered. The following experiments were performed with this aqueous colourless filtrate:

EXPERIMENT	OBSERVATION	INFERENCE
Test for Nitrogen : To a portion of the filtrate, a few crystals of FeSO_4 were added. (Alternatively freshly prepared FeSO_4 solution may also be added.) The mixture was boiled gently and then acidified with dilute H_2SO_4 .	A deep blue solution or precipitate	Nitrogen present.
Test for Sulphur : To a portion of the filtrate, 1-2 drops of dilute sodium nitroprusside solution was added.	Purple colouration	Sulphur present.
Test for halogens (If N and/or S absent): A portion of the filtrate was acidified with concentrated HNO_3 , boiled for 2-3 minutes, cooled and AgNO_3 solution was added. To the precipitate dilute NH_4OH was added.	Curdy white precipitate. Soluble, but reappeared on acidification with dilute HNO_3	Chlorine present.
If N and/or S present: A portion of the filtrate was acidified with concentrated HNO_3 and gently boiled till the volume of the solution becomes half. It was then cooled and AgNO_3 solution is added. To the precipitate dilute NH_4OH was added.	Same observation as above	Same inference as above

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Use of Zn & Na₂CO₃ mixture instead of metallic Na [Middleton's test]

[An intimate mixture of Zn dust and Na₂CO₃ (2 : 3 by weight) may be stored in a bottle.]

A pinch of organic sample and the above mixture (200 mg) was heated gently and then strongly to red hot on a non-luminous flame for about three minutes. Then the fusion tube was plunged in a mortar containing **distilled water** (6-7 mL). The mixture was ground thoroughly by a pestle and filtered. The following experiments were performed with this aqueous filtrate:

[When an organic compound is heated with a mixture of zinc powder and Na₂CO₃, the nitrogen and chlorine are converted into NaCN and NaCl respectively, and the sulphur into ZnS (insoluble in water). NaCN and NaCl are extracted with water and detected as in **Lassaigne's method**, whilst ZnS in the residue is decomposed with dilute HCl and H₂S evolved is identified with lead acetate paper which forms black PbS.]

Solubility Classification :

Observations to be made at room temperature

(scale: 100 mg of sample in 3 mL of solvent)

water	5% HCl	5% NaOH	5% NaHCO ₃	Conclusion
+	NP	NP	NP	Polar compound: low MW aliphatic acids, polyphenols, salts.
—	+	—	—	Basic : amines
—	—	+	+	Strongly acidic : acids, nitrophenols
—	—	+	—	Weakly acidic: phenols, imide
—	+	+	+	Bipolar compounds; may contain both amine and carboxylic acid groups, e.g. amino acids, sulphanilic acids etc.
—	—	—	—	Neutral compounds: a) carbonyl (if N absent) b) Nitro/amide (if N present)
‘+’ means soluble; ‘—’ means insoluble; ‘NP’ means not performed				

If the sample is soluble in water, then there is no need to check the solubility in all other aqueous solvents mentioned above. Report ‘NP’ (not performed) in the columns of other solvents.

Detection of Functional Groups by Systematic Chemical Analysis:

[If nitrogen is present as special element then tests for all the functional groups must be performed.]

CHP 34b

If nitrogen is absent as special element, then report as given below:

"Since nitrogen is absent as special element, tests for nitrogen containing functional groups aromatic amino ($-\text{NH}_2$), aromatic nitro ($-\text{NO}_2$), carboxamide ($-\text{CONH}_2$) and imide ($-\text{CONHCO}-$) are not performed".

[Perform only the tests for non-nitrogenous functional groups.]

Tests for Nitrogen Containing Functional Groups:

(aromatic $-\text{NH}_2$, aromatic $-\text{NO}_2$, $-\text{CONH}_2$ and $-\text{HNCONH}-$)

EXPERIMENT	OBSERVATION	INFERENCE
Test for aromatic $-\text{NH}_2$ (azo dye test): To 1 mL dilute HCl solution / suspension of the sample, 1 mL 2% NaNO_2 solution was added under ice cold condition. This cooled diazotized solution was then added to a previously cooled alkaline solution of β -naphthol.	Red/orange azo dye	Aromatic $-\text{NH}_2$ present.
Test for aromatic $-\text{NO}_2$ (in absence of aromatic $-\text{NH}_2$) Reduction followed by azo dye test: A few pieces of Zn or Sn granules were added to the sample (~50 mg) in concentrated HCl (2 mL). The mixture was boiled gently for 2 minutes. It was then cooled and filtered and diluted with water. Azo dye test as described above was performed with it.	Red/orange azo dye	Aromatic $-\text{NH}_2$ present.
Test for aromatic $-\text{NO}_2$ (in presence of aromatic $-\text{NH}_2$) However, Mulliken and Barker test can be performed for aromatic $-\text{NO}_2$ group whether or not aromatic $-\text{NH}_2$ group is present in the given sample. Mulliken and Barker test: To a mixture of sample (~50 mg), Zn dust (100 mg) and solid NH_4Cl (100 mg) 50% aqueous ethanol (3 mL) was added. The mixture was boiled gently in a water bath for 5 minutes and then filtered into freshly prepared Tollens' reagent (2 mL).	A grey/black precipitate or silver mirror	Aromatic $-\text{NO}_2$ present.

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Test for amide ($-\text{CONH}_2$) and imide: A mixture of the sample (~50 mg), 2-3 NaOH/KOH pellets and a few drops of water was heated strongly.	Smell of NH_3 was perceived and the evolved vapour turned phenolphthalein paper temporarily pink.	Amide or imide present.
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Preparation of Tollens' reagent, $\text{Ag}(\text{NH}_3)_2\text{OH}$:

A few drops of dilute NaOH solution are added to 1-2 mL of AgNO_3 solution. The resulting precipitate is then dissolved by adding requisite amount of NH_4OH solution.

Tests for Non-nitrogenous Functional Groups :

(phenolic $-\text{OH}$, $>\text{CO}$, $-\text{COOH}$)

EXPERIMENT	OBSERVATION	INFERENCE
Alcoholic solution of the sample is tested with moist blue litmus paper.	Blue litmus paper turns red.	strongly acidic functionality ($-\text{COOH}$) present.
1. Test for carboxylic acid ($-\text{COOH}$) : Sample or its alcoholic solution was added to a saturated solution of NaHCO_3 . Esterification: A solution of the sample in dehydrated alcohol (2 mL) and 2 drops of concentrated H_2SO_4 was warmed on a water bath for 5 minutes. It was cooled and then poured cautiously in a beaker containing 5% solution of NaHCO_3 (10-15 mL).	Effervescence of CO_2 was observed. Characteristic fruity smell of ester was perceived.	Acidic functionality ($-\text{COOH}$) present. Carboxylic acid group ($-\text{COOH}$) present.
2. Test for carbonyl ($>\text{CO}$ or $-\text{CHO}$) <i>(Aldehyde/Ketone):</i> 2,4-Dinitrophenylhydrazine (2,4-DNP) reagent (Brady's reagent) was added to a saturated alcoholic solution of the sample (2 mL). The mixture was shaken vigorously for few minutes and then the inner wall of the test tube was scratched with a glass rod. The reaction mixture may be heated on a water bath if necessary for 5 minutes	Orange/yellow crystalline precipitate.	Carbonyl group ($>\text{CO}$) present. Distinction between aldehyde & ketone may be done by Tollens' reagent.

<p>3. Test for phenolic –OH group:</p> <p>(a) To an alcoholic/aqueous solution of the sample, few drops of neutral FeCl₃ solution is added.</p> <p>(b) Back Dye Test: To a solution of 1 drop of aniline in dilute HCl, 1 mL 2% NaNO₂ solution was added under ice cold condition. The resulting solution was then added to cold alkaline solution of the sample.</p> <p><i>[Any one of the above tests, if positive, indicates the presence of phenolic –OH group. To show the absence, both the tests must be performed.]</i></p>	<p>Permanent or transient purple/red/blue/violet/green colouration.</p> <p>Red precipitate or colouration of azo dye observed.</p>	<p>Phenolic –OH group present.</p> <p>Phenolic –OH group present.</p>
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[According to the syllabus, however, ONLY ONE TEST FOR EACH FUNCTIONAL GROUP is to be reported]

Some Solid Organic Compounds for Qualitative Analysis in the Laboratory

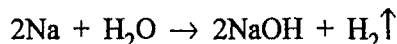
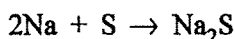
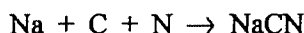
Succinic acid, Benzoic acid, Phenylacetic acid, Phthalic acid, Cinnamic acid, *p*-Anisic acid, *o*-Chlorobenzoic acid, Sulphanilic acid, Resorcinol, Hydroquinone, 2-Naphthol, Salicylic acid, *p*-Hydroxybenzoic acid, Vanillin, Benzil, Benzophenone, Benzoin, *p*-Chlorobenzaldehyde, *p*-Hydroxybenzaldehyde, *p*-Nitrobenzaldehyde, *p*-Toluidine, *p*-Anisidine, Aniline hydrochloride, *p*-Chloroaniline, *m*-Dinitrobenzene, *p*-Nitrotoluene, *p*-Nitrophenol, *p*-Nitroaniline, *o*-Nitroaniline, *m*-Nitroaniline, *p*-Nitrobenzoic acid, *m*-Nitrobenzoic acid, *p*-Aminobenzoic acid, Benzamide, Salicylamide, Phthalamide, Phthalimide, Sulphanilamide, Urea.

Reactions of the Tests for Detection of Nitrogen, Sulphur and Chlorine in an Organic Sample

Organic compounds containing nitrogen, sulphur or halogens when fused with sodium metal, a reductive decomposition of the compound takes place. The elements are converted to sodium salts of inorganic ions like CN[–], SCN[–], S^{2–} and X[–] (Cl[–], Br[–], I[–]).

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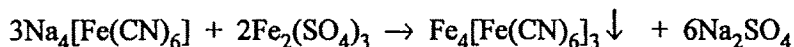
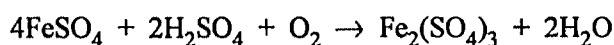
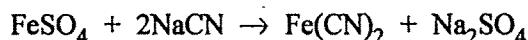
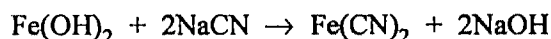
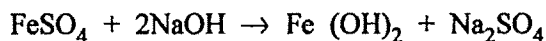
C, N, S, X (halogen) $\xrightarrow{\text{Fusion with sodium}}$ NaCN, NaSCN, Na₂S, NaX.



All these are present in the aqueous filtrate.

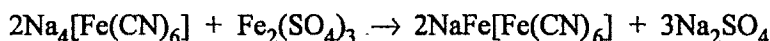
(i) Test For Nitrogen :

(a) **Lassaigne Test** : 2 mL filtrate + few drops of freshly prepared FeSO₄ solution; a dark green precipitate of Fe(OH)₂ is obtained. If 'S' is present in the sample, the precipitate will be black. For such cases, more FeSO₄ solution is added and the mixture is heated to boiling and then dilute H₂SO₄ is added and cooled when immediate appearance of **blue or green precipitate** or colour of **Prussian blue**, Fe₄[Fe(CN)₆]₃ or NaFe[Fe(CN)₆] indicates the presence of nitrogen.



Prussian Blue (blue precipitate)

OR

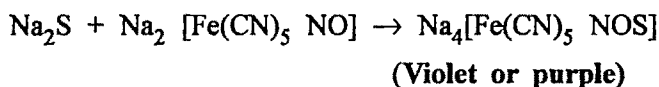


Prussian Blue (blue solution)

(b) **Middleton's Test**: When an organic compound is heated with a mixture of zinc powder and Na₂CO₃, the nitrogen and chlorine are converted into NaCN and NaCl respectively, and the sulphur into ZnS (insoluble in water). NaCN and NaCl are extracted with water and detected as in **Lassaigne's method**, whilst ZnS in the residue is decomposed with dilute HCl and H₂S evolved is identified with lead acetate paper which forms black PbS. The test for nitrogen is thus not affected by the presence of sulphur; this constitutes an advantage of the method. [Ref: *Qualitative Organic Analysis, 2nd Edition, A.I. Vogel, (Part-2)* pages: 41-42]

(ii) Test for Sulphur: [Sodium Nitroprusside Test]

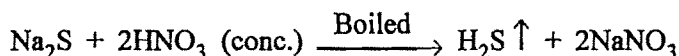
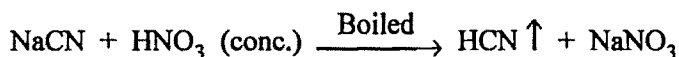
2 mL of filtrate of the sodium extract +1 -2 drops of freshly prepared aqueous solution of sodium nitroprusside; appearance of **violet or purple colour** confirms the presence of sulphur.



(iii) Test for Halogens:

Cyanide (CN^\ominus) and sulphide (S^{2-}) ions, if present must be removed, since they interfere the tests with AgNO_3 solution.

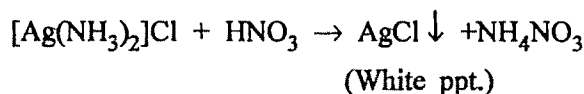
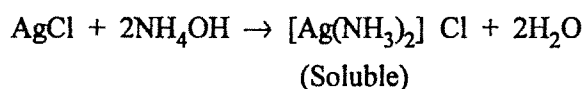
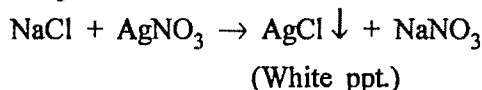
Acidify the sodium extract with concentrated HNO_3 and **boiled** to reduce the volume to **half** of the original to drive off HCN and H_2S gases formed.



The acidified solution (filtrate) was taken and AgNO_3 solution was added:

Test for Chlorine:

Observation: White precipitate, soluble in ammonium hydroxide solution which reappears on addition of concentrated HNO_3 .



DETECTION OF FUNCTIONAL GROUPS :

1. Carboxylic acid group : ($-\text{COOH}$)
2. Phenolic hydroxyl group : ($\text{Ar}-\text{OH}$)
3. Carbonyl group : (ketonic $>=\text{O}$ or aldehydic $-\text{CHO}$ group)
4. Aromatic primary amino group : ($\text{Ar}-\text{NH}_2$)
5. Aromatic nitro group : ($\text{Ar}-\text{NO}_2$)
6. Amido or imido group : ($-\text{CONH}_2$ or $-\text{CONHCO}-$)

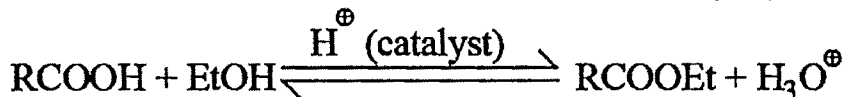
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1. Carboxylic Acid Group [–COOH group] :

- (a) Aqueous solution, aqueous suspension or ethanolic solution of the compound is treated with moist blue litmus paper; if **turns red**, presence of –COOH group may be suspected.
- (b) Saturated solution of NaHCO_3 + a pinch of sample/ethanolic solution of the sample; **Effervescence of CO_2** occurs, –COOH may be present. Effervescence of CO_2 is also possible by $-\text{SO}_3\text{H}$ group or activated phenols like nitrophenols, or polyhydroxyphenols or amine hydrochlorides.

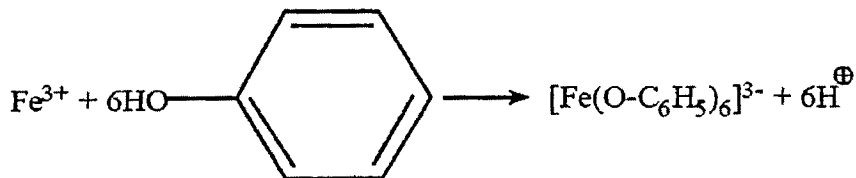


- (c) Esterification test : Small amount of sample + 2 mL ethyl alcohol + 2–3 drops of concentrated H_2SO_4 , heated on a water bath for 5 minutes followed by pouring into 20 mL saturated bicarbonate solution; if **fruity smell of ester** comes, **COOH group confirmed**.



2. Phenolic Hydroxyl Group [ArOH]:

- (a) Alcoholic solution of the sample + 2 drops of neutral FeCl_3 ; **characteristic permanent or transient purple/red/blue/violet/green colour appeared**.



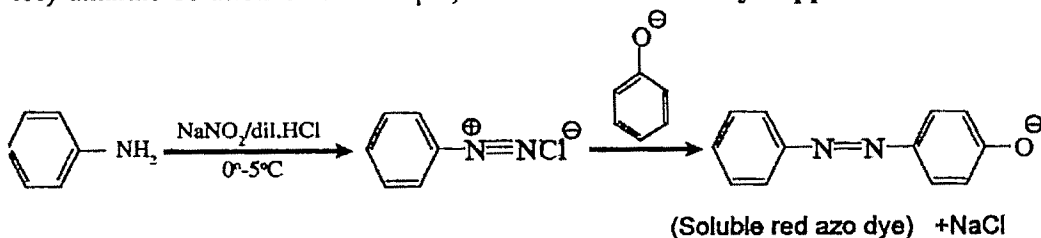
N.B.: * β -Naphthol gives **green** colouration.

** Hydroquinone gives **Transient green** colour which turns **red** ultimately.

*** *m*- and *p*-hydroxybenzoic acids give **wine red** colouration.

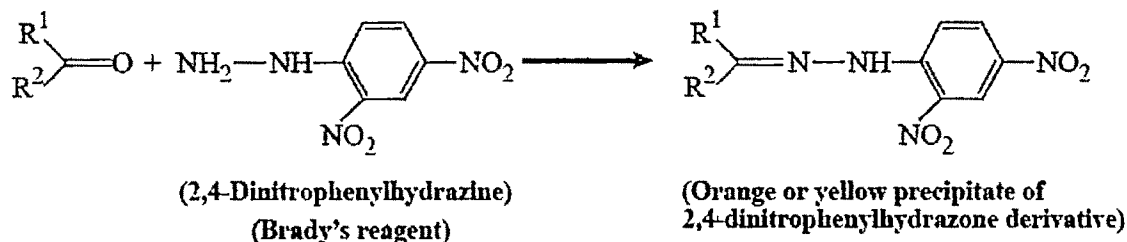
**** α -Naphthol, *o*-nitrophenol, *o*- and *m*-aminophenol, 2,4 -diaminophenol **do not** respond to this test.

- (b) **Back dye test:** (1 drop of aniline in dil. HCl + few drops of freshly prepared aqueous NaNO_2 solution cooled to $0^\circ\text{--}5^\circ\text{C}$ in a test tube. Contents of the test tube were added to cooled (in ice) alkaline solution of the sample; a **brilliant red azo dye** appeared.



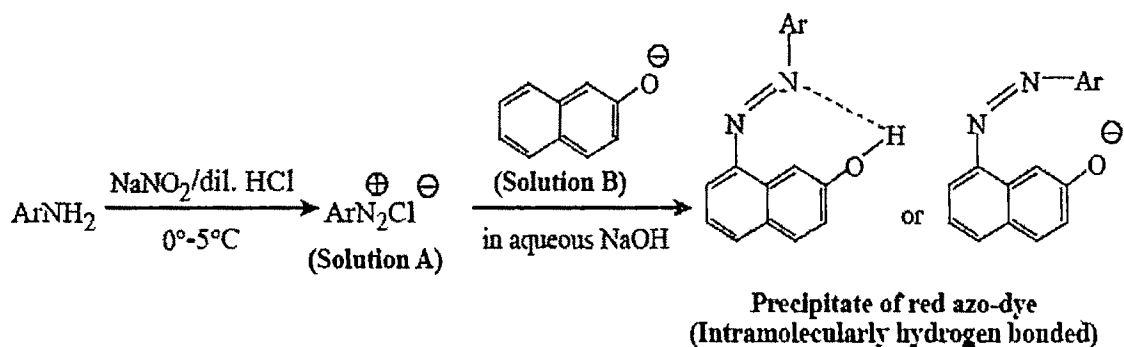
3. Carbonyl Group ($>=O$) [Both $-CHO$ and $>C=O$] groups]:

(a) Alcoholic solution of the sample + equal volume of 2,4-DNP heated on a water bath (if necessary) for 5 minutes and the sides of the test tube are scratched if necessary; **orange or yellow precipitate**.



4. Primary Aromatic Amino Group [$ArNH_2$]:

Sample + dilute HCl + freshly prepared aqueous $NaNO_2$ solution, cooled to $0^\circ - 5^\circ C$ (**diazotized solution A**); cold alkaline solution of β -naphthol was prepared (**β -naphthol dissolved in dilute aqueous NaOH solution; solution B**); the diazotized **solution A** was poured into **solution B**; a **brilliant red azo dye** appeared.

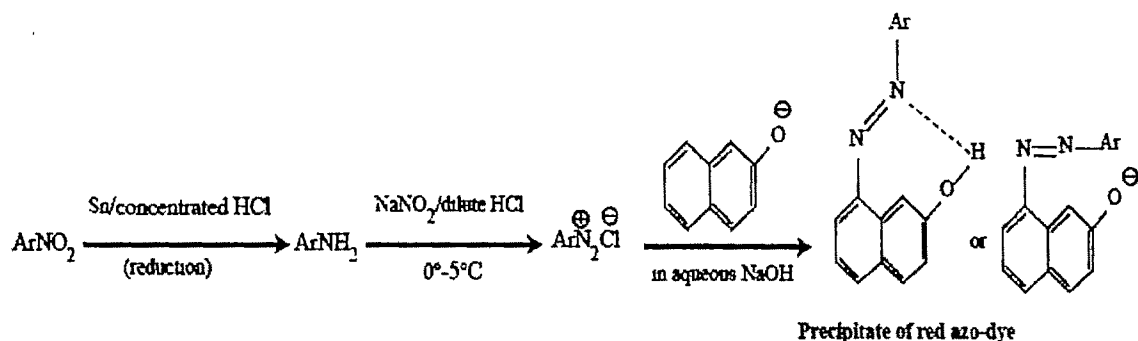


5. Aromatic $-NO_2$ Group:

(a) **Reduction of $ArNO_2$ to $ArNH_2$** (should be done when $ArNH_2$ group is absent in the sample) [**Diazo coupling reaction**]:

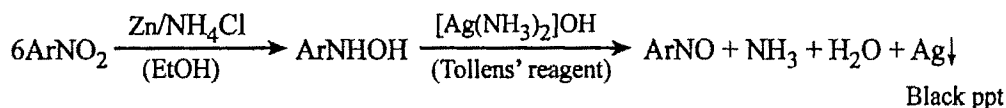
Sample + metallic Sn + 1 mL concentrated HCl, **boiled for 5 minutes**, cooled, diluted with 5 mL water, filtered and cooled to 0° to $5^\circ C$ in ice + freshly prepared aqueous $NaNO_2$ solution, cooled to $0^\circ - 5^\circ C$ (**diazotized solution A**); cold alkaline solution of β -naphthol was prepared (**β -naphthol dissolved in dilute aqueous NaOH; solution B**); the diazotized **solution A** was poured into **solution B**; a **brilliant red azo dye** appeared.

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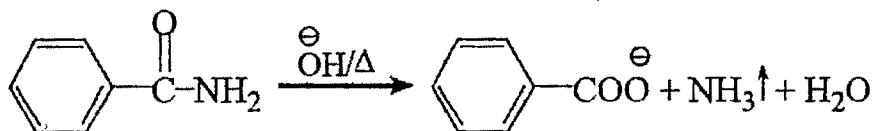
(b) Partial Reduction of ArNO_2 to ArNHOH (can be performed in presence of ArNH_2 group) : [Mulliken and Barker test]

Sample dissolved in ethanol + pinch of NH_4Cl + Zn dust + a few drops of water in a test tube, heated on a water bath for 5 minutes; filtered hot directly into **Tollens' reagent** (AgNO_3 + 1-2 drops of aqueous NaOH solution, dark grey/black precipitate of Ag_2O , then concentrated NH_4OH solution was added till a clear solution was obtained $[\text{Ag}(\text{NH}_3)_2]\text{OH}$. A **black precipitate** appeared which turned to **silver mirror** on heating on a water bath.



6. Test for Amide Group $[-\text{CONH}_2]$ or Imide Group $[\text{CONHCO}]$:

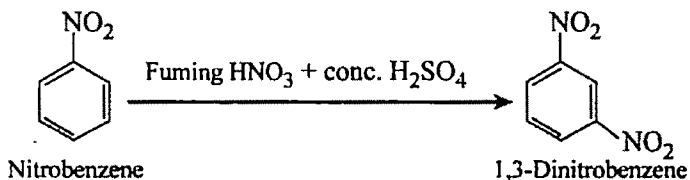
Sample + 2-3 solid beads of NaOH + 2-3 drops of water and heated gently; a moist **red litmus paper** held at the mouth of the test tube which **turned blue** or glass rod moistened with concentrated HCl held at the mouth of the test tube, **white fumes** of NH_4Cl appeared. The evolved NH_3 gas also turned phenolphthalein paper temporarily pink.



ORGANIC PREPARATIONS

1. Nitration of Organic Compounds

A. Nitration of Nitrobenzene to 1,3-Dinitrobenzene :

*Procedure :*

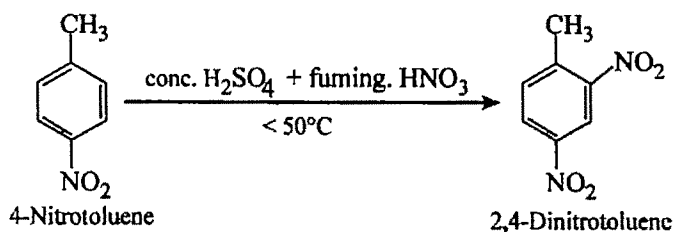
Place concentrated sulphuric acid (7 mL) and fuming nitric acid (5 mL) in a 100 mL **dry** conical flask. Add slowly, in portions (~ 1 mL at a time), 5 mL nitrobenzene into the above acid mixture. After each addition shake the flask well to ensure thorough mixing of the liquids. Attach an air condenser at the mouth of the flask. Heat the mixture, with frequent shaking, on a boiling water bath for 30 minutes (or until a drop of the reaction mixture readily solidifies on pouring into water taken in a test tube). Allow the mixture to cool somewhat and pour it cautiously with vigorous stirring into about 100 ml of ice cold water. Filter the solid under suction, wash thoroughly with **cold** water until the washings are acid free, dry in the air and **record the yield**.

Crystallise a portion of the crude product from **rectified spirit** and note the **melting point**.

Yield : ~ 5 g

M.P.: 89°C–90°C

B. Nitration of 4-Nitrotoluene to 2,4-Dinitrotoluene :



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Procedure:

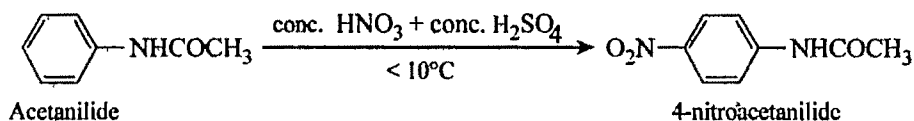
Place fuming nitric acid (3 mL) and concentrated sulphuric acid (4 mL) and a small piece of unglazed porcelain in a 100 mL dry conical flask. Add gradually, in small portions, 3.5 g of 4-nitrotoluene into the acid mixture keeping the temperature of the reaction mixture below 50°C. Cool the flask if necessary by immersing it in cold water. Place a small funnel at the mouth of the flask and heat on a water bath at 90°C–95°C for 30 minutes. Allow to cool to room temperature and pour the reaction mixture slowly into 125 mL ice cold water. Filter the crude 2,4-dinitrotoluene under suction, wash thoroughly with cold water till acid free and drain well. Dry the product in air on a filter paper and **record the yield**.

Crystallise a portion of the crude product from **minimum amount of hot methanol** and record the **melting point**.

Yield: ~ 3g.

M.P.: 71°C

C. Nitration of Acetanilide to 2,4-Nitroacetanilide :



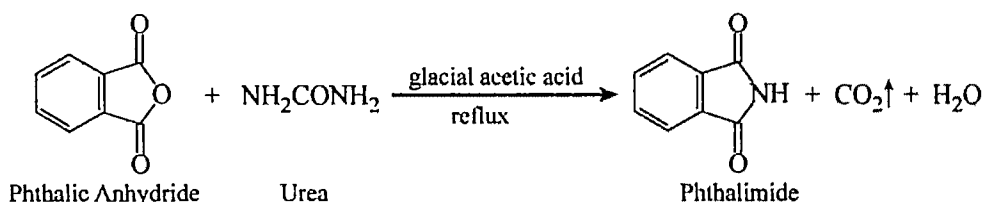
Procedure:

Place glacial acetic acid (5 mL) and 5 g of acetanilide in a beaker. Add concentrated sulphuric acid (10 mL) with stirring. The mixture becomes warm and a clear solution results. Surround the beaker with a freezing mixture of ice and salt and place a thermometer (110°C range) in the beaker. When the temperature falls to 0°C – 2°C, add **dropwise with stirring** a cold mixture of concentrated nitric acid (2.5 mL) and concentrated sulphuric acid (1.5 mL), maintaining the temperature below 10°C. After all the mixed acid has been added, remove the beaker from the freezing mixture and allow it to stand at room temperature for 1 hour. Pour the reaction mixture onto 50 g of crushed ice with stirring. Filter the resulting solid under suction, wash thoroughly with **cold water** until free from acid and drain well. **Record the yield** of the crude product.

Crystallise a portion of the crude pale yellow product from **rectified spirit**, wash with little **cold alcohol** and dry on a steam bath. *p*-Nitroacetanilide appears as colourless crystals and record the **melting point**.

Yield: ~ 4g

M.P.: 214°C

2. Condensation Reactions:**A. Preparation of Phthalimide from Phthalic Anhydride and Urea :****Procedure:**

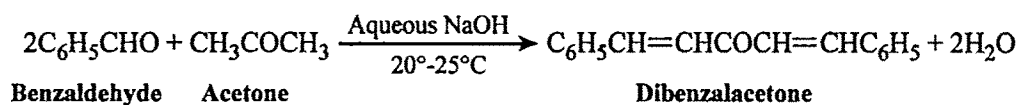
Place phthalic anhydride (5 g), urea (2.5 g) and glacial acetic acid (10 mL) in a **dry** 100 mL round bottomed flask fitted with a reflux condenser. Add a small piece of unglazed porcelain and heat under reflux for 1 hour. Cool to room temperature and add 20-30 mL of water to disintegrate the solid in the flask. Filter the product under suction, wash thoroughly with water until free from acid, drain well and dry on a steam bath. **Record the yield** of the crude product.

Crystallise a portion of the crude product from **hot water** and note the **melting point** of the crystallised product.

Yield: ~ 4.8 g

M.P.: 233°C–234°C (>200°C)

N.B.: Phthalimide often comes as crystals which are practically pure, so further crystallization is not necessary.

B. Preparation of Dibenzalacetone by Claisen–Schmidt Reaction :**Procedure:**

Prepare a cold solution of 2.5 g of sodium hydroxide in 25 mL of distilled water and 20 mL of ethanol in a 150 ml conical flask. In a **dry** test tube prepare a mixture of 2.5 mL of freshly distilled benzaldehyde and 1 mL of analytical grade acetone. Add the mixture from the test tube into the cold solution in the conical flask. Shake frequently and keep the temperature at 20°C–25°C for 15 minutes by immersing the flask in a bath of ice cold water. Filter the precipitated dibenzalacetone under suction, wash with cold water to remove the alkali and dry the solid at room temperature upon the filter paper. **Record the yield** of the crude product.

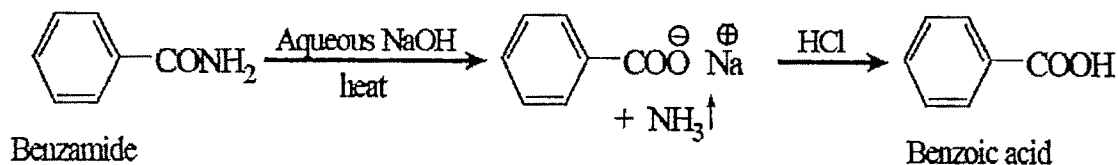
Crystallise the crude product from **hot rectified spirit**. Dibenzalacetone appears as pale yellow crystalline needles. **Record the melting point** of crystallised solid.

Yield: ~ 2.2 g

M.P.: 112°C

3. Hydrolysis of amides/ Imides/ Esters

A. Hydrolysis of Benzamide to Benzoic Acid:



Procedure:

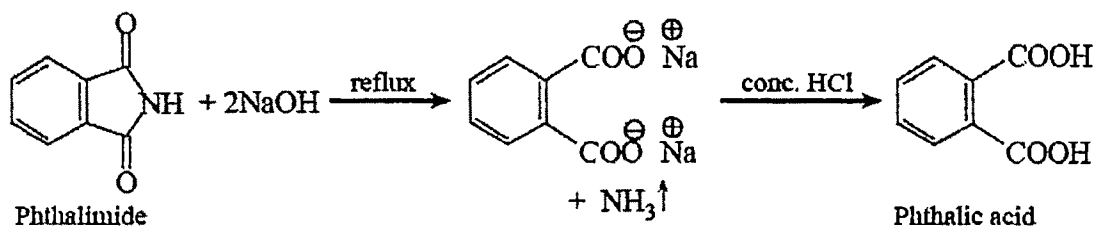
Place 5 g of benzamide and 50 mL of 10% NaOH solution in a 250 mL round bottomed flask fitted with a reflux condenser. Add a small piece of unglazed porcelain and boil the mixture gently under reflux for 30 minutes on asbestos-centred wire gauze. Then detach the condenser and continue boiling for another 2-3 minutes. Cool the flask under tap water and pour the reaction mixture in a 250 mL beaker. Acidify strongly with concentrated HCl, cool the content to room temperature and filter the solid under suction. Wash the solid with **cold water**, drain well and dry on a steam bath. Record the yield.

Crystallise a portion of the crude product from **hot water**. Note the **melting point** of the crystallised product.

Yield : ~ 3 g

M.P.: 122°C

B . Hydrolysis of Phthalimide to Phthalic Acid :



Procedure :

Place 5 g phthalimide and 50 mL of 20% sodium hydroxide solution in a round bottomed flask fitted with a reflux condenser. Add a small piece of unglazed porcelain and boil the mixture gently under reflux on asbestos-centred wire gauze for 30 minutes. Then detach the condenser and continue boiling for another 3-4 minutes. Cool the flask under tap water and pour the reaction mixture in a 250 mL beaker. Acidify strongly with concentrated HCl, cool the content to room temperature and filter the solid under suction. Wash the solid with **cold water**, drain well and dry on a steam bath. **Record the yield.**

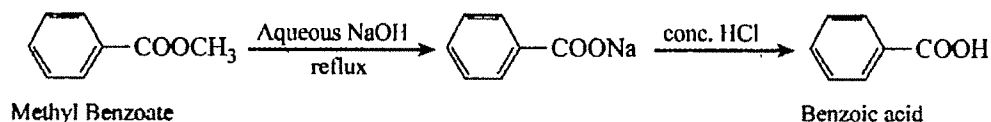
CHP 34b

Crystallise a portion of the crude product from hot water and note the melting point of the crystallised product.

Yield: ~ 3.5 g

M.P.: 195°C

C. Hydrolysis of Methyl Benzoate to Benzoic Acid:



Procedure :

Place 5 ml of methyl benzoate and 50 mL of 20% sodium hydroxide solution in a 250 ml round bottomed flask fitted with a reflux condenser. Add a small piece of unglazed porcelain and boil the reaction mixture gently under reflux for 1 hour until the oil has disappeared. Then detach the condenser. Cool the reaction mixture to room temperature and filter the solid under suction. Wash the solid with cold water and drain well. Dry on a steam bath and record the yield.

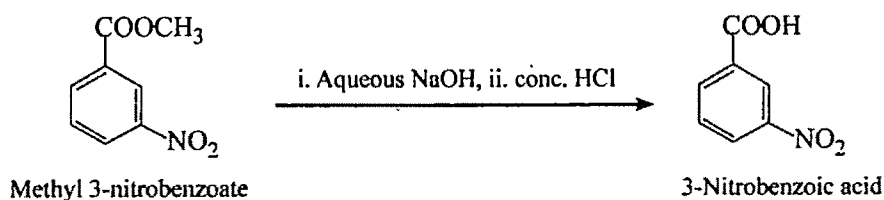
Crystallise a portion of the crude product from hot water and note the melting point.

Yield: ~ 2 g

M.P.: ~ 122°C

N.B.: Follow the above procedure for the hydrolysis of ethyl benzoate.

D. Hydrolysis of Methyl 3-Nitrobenzoate to 3-Nitrobenzoic Acids :



Procedure:

Place 6 g of methyl 3-nitrobenzoate and a solution of 3 g of sodium hydroxide in 15 mL of water in a 100 mL round bottomed flask equipped with a reflux condenser. Heat the mixture to boiling during 5-10 minutes until the ester disappears. Dilute the reaction mixture with an equal volume of water. Cool the diluted reaction mixture and pour it with vigorous stirring into 10 mL of concentrated HCl. Allow to cool to room temperature by holding the flask under tap water. Filter the crude 3-nitrobenzoic acid under suction, wash the solid with water and drain well. Dry on a steam bath and record the yield.

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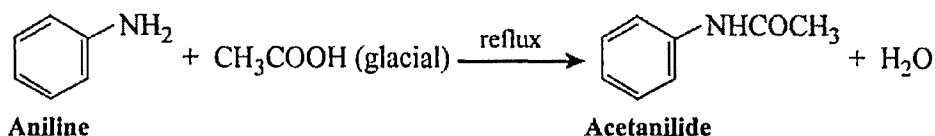
Crystallise the crude 3-nitrobenzoic acid from 1% HCl. The pure acid is a pale cream yellow solid. Note the **melting point** of the crystallised product.

Yield: ~5.5 g

M.P.: 141°C

4. Acetylation of Aromatic Amines/Phenols:

Acetylation of Aniline to Acetanilide :



Procedure:

Place 5 mL of aniline and glacial acetic acid (15 mL) in a 100 mL **dry** round bottomed flask. Add a small piece of unglazed porcelain. Attach a **dry** reflux condenser at the mouth of the flask and heat the reaction mixture under reflux for 45 minutes. Cool the reaction mixture and pour it in thin stream to 150 g crushed ice water mixture taken in a beaker, with stirring. Filter the solid under suction and wash with **cold** water, drain and dry the solid on steam bath. **Record** the yield of the crude product.

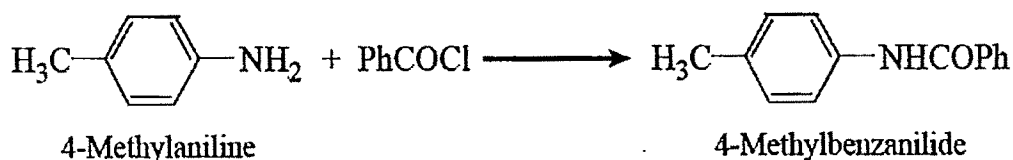
Crystallise a portion of the crude product from **hot** water and note the **melting point** of the crystallised product.

Yield: ~ 3 g.

M.P.: 114°C

5. Benzoylation of Aromatic Amines/Phenols:

A. Benzoylation of 4-Methylaniline (*p*-Toluidine) to 4-Methylbenzanilide:



Procedure :

Take a solution of 4-methylaniline (2 g) in acetone (15 mL) and 40 mL of brine (saturated solution of sodium chloride in water) in a 250 mL Erlenmeyer flask. To the above mixture, add a solution of benzoyl chloride [PhCOCl] (3 mL) in acetone (10 mL), **dropwise** with **stirring** and continue the stirring for about 5-10 minutes. Finally pour the whole mixture into saturated solution of NaHCO3 (100 mL) taken in a 500 mL beaker, stir well and filter under suction. Dry the product on a steam bath and **record** the yield.

CHP 34b

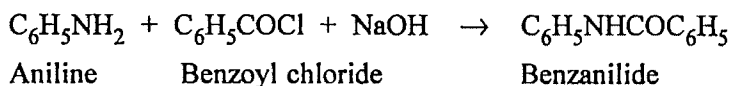
Crystallise a portion of the crude product from **aqueous alcohol** and note the **melting point**.

Yield: ~ 3 g

M.P.: 158°C

N.B.: The method is also applicable to prepare benzoate esters of amino acids. In case of amino acids, acidification by concentrated HCl is required after bicarbonate treatment.

B. Benzoylation of Aniline to Benzanilide by *Schotten-Baumann* Reaction:



Procedure :

Place a solution of aniline (3 mL) in acetone and 30 mL of 10% aqueous sodium hydroxide in a 150 mL conical flask and add 4.5 mL of benzoyl chloride in portions. Stopper the flask and shake the flask vigorously for 10-15 minutes while opening the stopper occasionally to release the pressure inside the flask. The crude benzanilide separates as white solid. When the reaction is complete, (*i.e.* when no odour of benzoyl chloride is perceived. **Caution : Eye Irritating!**) make sure that the reaction mixture is alkaline. Filter the product under suction, wash thoroughly with water and drain well. Dry the crude solid on a steam bath and **record the yield** of the crude product.

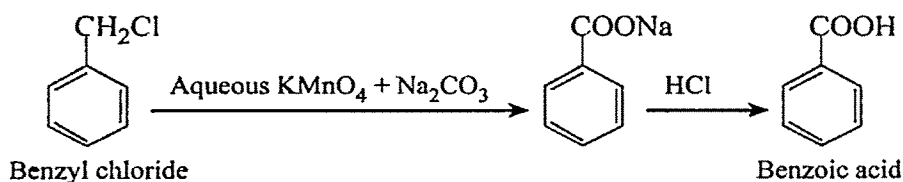
Crystallise a portion of the crude product from **hot rectified spirit** (filter the hot solution under suction through a preheated Buchner funnel, if necessary). Collect the colourless crystals of benzanilide, dry on a steam bath and note the **melting point**.

Yield: ~ 5.5 g

M.P.: 162°C

6. Side Chain Oxidation of Aromatic Compounds :

A. Oxidation of Benzyl Chloride to Benzoic Acid:



Procedure :

Place benzyl chloride (4.5 mL), Na_2CO_3 (4 g), KMnO_4 (9 g) and 200 mL of water and a few

Practical Work Book Chemistry (Honours)

boiling chips in a 500 mL round bottomed flask fitted with a reflux condenser**. Boil the mixture gently for 1 hour, cool the reaction mixture, filter the brown precipitate of MnO_2 , acidify the filtrate with concentrated HCl and add a pinch of NaHSO_3 with stirring until the brown colour of MnO_2 completely disappears and only a white precipitate remains. After cooling, filter the solid under suction and wash with cold water and drain well. Dry on a steam bath and **record the yield** of the crude product.

Crystallise a portion of the crude product from **boiling water** and note the **melting point** of the crystallised product.

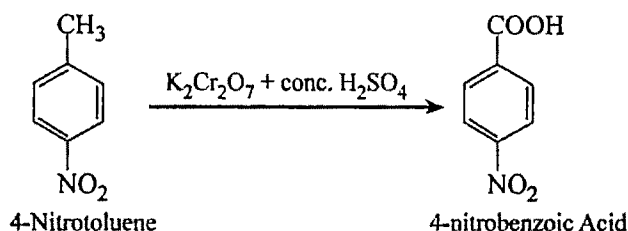
Yield: ~ 3.5 g

M.P.: 122°C

** To avoid bumping, the round bottomed flask should be fitted slightly slanted and a small stick of the length of the round bottomed may be introduced in it.

N.B.: Oxidation of toluene to benzoic acid can be done by following the same method.

B. Oxidation of 4-Nitrotoluene to 4-Nitrobenzoic Acid :



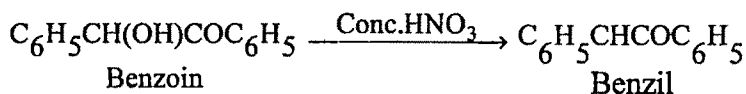
Procedure:

In a 250 mL round bottomed flask, take water (30 mL), concentrated H_2SO_4 (20 mL) and then $\text{K}_2\text{Cr}_2\text{O}_7$ (15 g). To the above warm solution, add 5 g of 4-nitrotoluene in portions with swirling during 5 minutes. Swirl the mixture for another 5 minutes. Attach a reflux condenser to the round bottomed flask and boil the mixture gently under reflux for 30 minutes. Transfer the hot mass in a 250 mL beaker and break the lump while hot. Cool the mixture to room temperature and add slowly to it 100 mL of ice cold water. Filter the solid under suction and wash thoroughly with cold 5% aqueous H_2SO_4 . Drain well and dry the crude solid on a steam bath. **Record the yield** of the crude product.

Dissolve 1/4th of the crude product in minimum volume of saturated aqueous NaHCO_3 solution. Warm it with a pinch of decolourising charcoal, cool to room temperature and filter through a fluted filter paper. Acidify the filtrate with 15% aqueous H_2SO_4 . Collect the purified product, wash with a little cold water, drain well and dry on a steam bath. Note the **melting point** of the purified product.

Yield: ~ 5 g

M.P.: 241°C (>200°C)

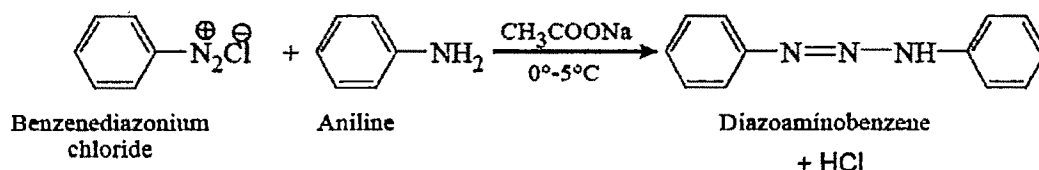
C. Oxidation of Benzoin to Benzil: (Not a Side Chain Oxidation)**Procedure:**

Place benzoin (4 g) and concentrated nitric acid (20 mL) in a 100 mL **dry** round bottomed flask. Attach an air condenser and heat the mixture with occasional shaking on a boiling water bath for one hour. Then detach the condenser and let the open flask stand for 3-4 minutes to allow escape of any brown fumes. Allow to cool and pour the reaction mixture to a beaker containing 75 mL of cold water and stir well until the oil solidifies completely as a yellow solid. Filter the crude product under suction, wash thoroughly with **cold** water to make it acid free, drain well, dry in the air and **record the yield**.

Crystallise a portion of the crude product from **rectified spirit** and note the **melting point** of the crystallised product.

Yield: ~ 3 g

M.P.: 95°C

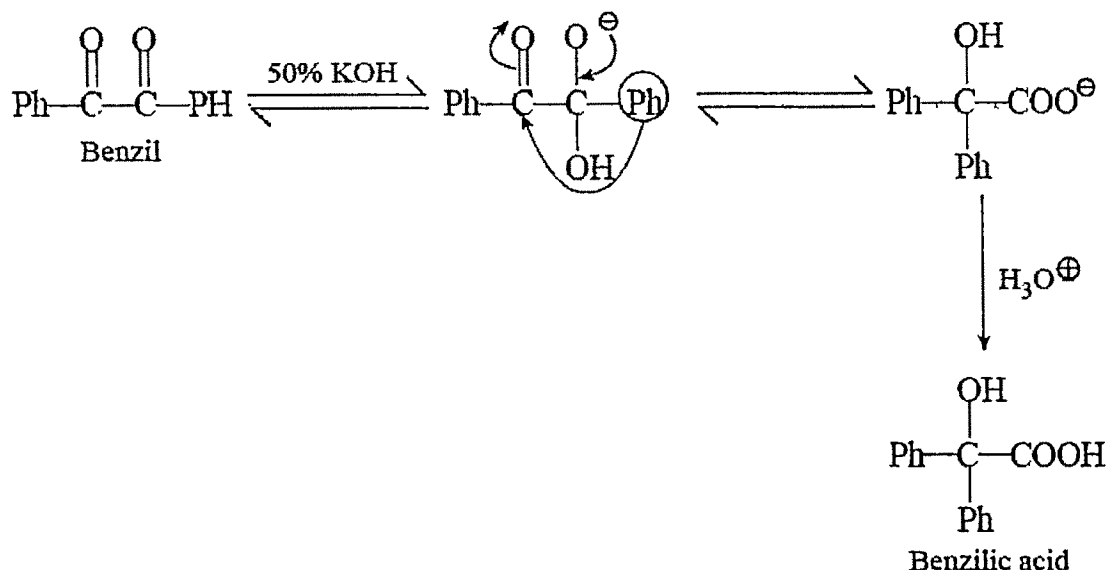
7. Diazo Coupling Reactions of Aromatic Amines :**Preparation of Diazoaminobenzene from Aniline by Diazo Coupling Reaction :****Procedure :**

Place 20 mL of water, 5 mL of concentrated HCl and 3.5 mL of freshly distilled aniline in a 100 mL conical flask. Shake the mixture thoroughly and add 15 g of crushed ice. To the above solution add a solution of 1.3 g of NaNO₂ in 4 mL of water with constant shaking during 5 minutes. Allow the mixture to stand with occasional shaking for 10 minutes and then add a solution of sodium acetate (5.3 g) in 10 mL of water during 5 minutes. A yellow precipitate of diazoaminobenzene starts to form at once. Allow the mixture to stand with occasional shaking for half an hour, keeping the temperature below 20°C (add ice if necessary). Collect the product by filtration under suction, wash with **cold** water (~50 mL), drain well and dry on a filter paper in the air. **Record the yield** of the crude product.

Crystallise a portion of the crude product from **light petrol** (60°C–80°C) [**Caution: Inflammable**] to obtain pure diazoaminobenzene.

Yield: ~ 3.5 g

M.P.: 97°C



II. Preparation of Benzilic Acid from Benzil in Solid Phase:

[Reference: Monographs on Green Chemistry–Laboratory Experiments. Page-21; Green Chemistry Task Force Committee, DST.]

Procedure :

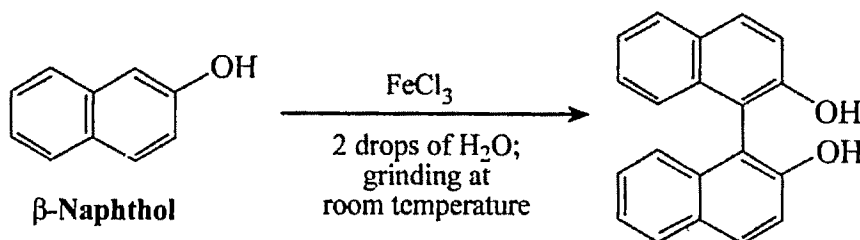
Grind 3 g of benzil thoroughly with 3 g of solid KOH (or solid NaOH) in a dry mortar with the help of a pestle to make an easy flowing powder. Take this powder in a 100 mL **dry** conical flask fitted with a piece of cotton at the mouth of the flask and heat it on a boiling water bath for 45 minutes. Allow the flask to cool to room temperature and dissolve the content of the flask in minimum volume of water. Remove unreacted benzil, if any, by filtration. Cool the aqueous solution well by keeping the flask in an ice bath. Now acidify the solution with concentrated HCl with thorough cooling in ice. Filter the precipitated crude benzilic acid under suction, wash it with a little **cold** water, drain well and dry on a steam bath. **Record the yield** of crude benzilic acid.

Crystallise a portion of the crude benzilic acid from **hot water** and note the **melting point** of the crystallised product.

Yield: ~ 2.5 g (~ 80%)

M.P.: 150°C

B. Oxidative Coupling of β -Naphthol :



Procedure:

Grind a mixture of β -naphthol (2.88 g) and iron (III) chloride (0.7 g) with 2 drops of water in an agate (or porcelain) mortar approximately for 20 minutes. Allow the mixture to stand for approximately 2 hours with a little grinding occasionally. Transfer the mixture with water (40 mL) into a 100 mL beaker and then boil for 10-15 minutes. Cool the mixture and filter the solid under suction, wash with boiling water (10 mL), dry and **record the yield** of the crude product. **Crystallise** a portion of the crude solid from **toluene**.

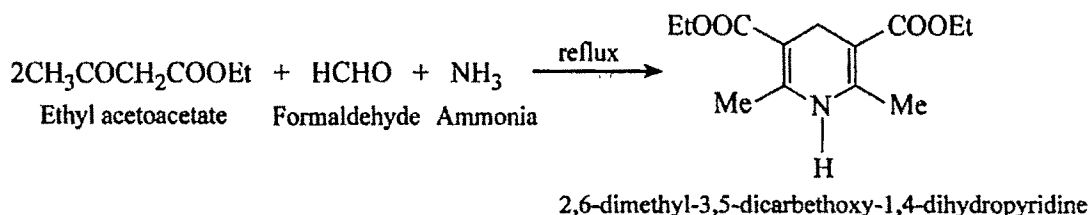
Yield: ~3.9 g (90%)

M.P.: 214°C–216°C (>200°C)

10. Green “Multi-Component-Coupling” Reaction :

A.Preparation of 2,6-Dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine

(HANTZSCH SYNTHESIS OF PYRIDINE)



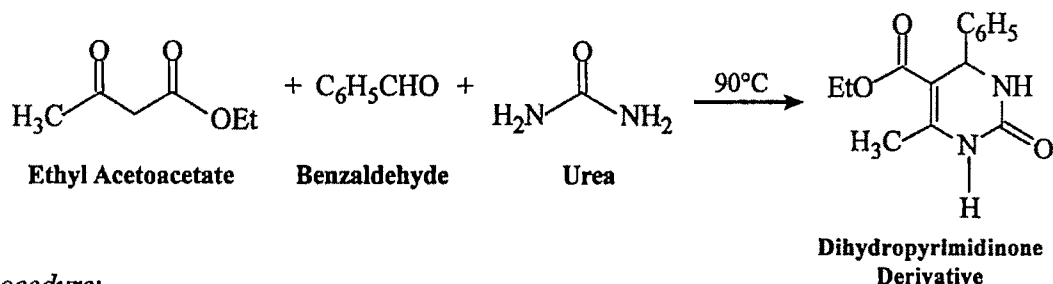
Procedure:

Take 40% HCHO (2.8 mL), ethyl acetoacetate (10 mL) and liquor ammonia (12 mL) in a 100 mL round bottomed flask fitted with a reflux condenser. Wash the sides of the condenser with 3.8 mL of EtOH and mix the contents of the flask thoroughly. Reflux the mixture on a steam bath for 2 hours and then cool in an ice bath. Filter the solid separated under suction, wash it carefully with **well cooled ethanol** (~10 mL) in several portions and drain well. Dry the crude pyridine derivative and **record the yield**.

Crystallise a portion of the crude product from **hot ethanol** as pale yellow crystalline solid and note the **melting point**.

Yield: ~ 9.5 g

M.P.: 181°C–183°C

B. Three Component Coupling:**Synthesis of Dihydropyrimidinone :***Procedure:*

Place benzaldehyde (2.2 g) (2.3 mL), ethyl acetoacetate (2.6 g) (2.5 mL) and urea (1.4 g) in a **dry** round bottomed flask or **dry** 100 mL conical flask. Shake the flask by hand for 2 minutes. Heat the reaction mixture in a water bath at 90°C for one hour. With progress of the reaction, a solid starts to deposit and after one hour the flask is full of solid. Take out the solid carefully with a spatula or spoon in a conical flask. Wash the yellow solid with **cold** water (1 mL) and **record the yield** of the crude product.

Crystallise a portion of the crude product from **rectified spirit** to give a colourless solid.

Yield: ~2 g (79%)

M.P.: 201°C–202°C (>200°C)

